STUDIES ON NEW PROCESSING AIDS AND OTHER COMPOUNDING INGREDIENTS IN SPECIAL PURPOSE RUBBERS

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by MOHAN VARGHESE under my supervision and guidance in the department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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DECLARATION

I hereby declare that the thesis entitled "Studies on new processing aids and other compounding ingredients in special purpose rubbers" is the original work carried out by me under the supervision of Dr. A. P. Kuriakose, Emeritus Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682022, and no part of this thesis has been presented for any other degree from any other institution.

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CHAPTER I

Chapter I

INTRODUCTION

A plasticiser is an important compounding ingredient incorporated into a polymer to increase its flexibility, softness, distensibility or workability. In addition to the above said functions plasticisers also help in forming and fabrication steps. Processing aids are a class of additives used specifically for assisting processing, which unlike plasticisers do not alter the end properties of the mixes to which they have been incorporated. However there are certain substances which function as processing aids in addition to their role as plasticisers. Plasticisers are generally classified into two groups, viz., external and internal plasticisers. The former does not form part of the polymer structure whereas the latter offers some structural modifications of the polymer thereby reducing its glass transition temperature (T_g). In the polymer industry external plasticisers are generally mentioned simply as plasticisers, and the process by which these materials function is described as external plasticisation as they do not chemically bind to the polymer.

In the early stages of the plasticiser technology camphor was occupying the centre stage as this natural product was widely being used for plasticising nitrocellulose. As long ago as 1901, the search for technically superior and price competitive substitutes for camphor resulted in the first patents for phthalate and phosphate esters as plasticisers[1,2]. In 1930's, when it was discovered that PVC could be processed safely at high temperatures by incorporating heat stabilisers as additives, it resulted in the rapid research for substances that could be used for plasticising PVC. By 1950, dioctylphthalate (DOP) had become the largest tonnage plasticiser with a small group of other similar phthalates. Now the largest single product used as plasticiser throughout the world is DOP. PVC industry accounts for more than 90% of the plasticisers used world over. The fortune of any plasticiser is heavily centred around the future of flexible PVC, as it is being widely perpetuated by environmentalist world over that the production, use and disposal of the material was causing serious damage to the environment. In such a situation it is imperative to note that future competitiveness of plasticised PVC is strongly dependent on the continued availability of cost effective plasticisers, which are not seen to pose unacceptable health, safety and environmental risks. This aspect justifies the search for other products as substitutes for conventional ester type plasticisers now being used by the industry. Processing aids is a generic term given to a class of material which, when added to a rubber compound at a relatively low loading, will improve processability without adversely affecting physical properties. Besides petroleum oils, other important processing aids for rubbers include waxes, tars, pitches, fatty acids, zinc soaps, homogenising resins etc. Their use in rubber compounds imparts such advantages like viscosity reduction, filler incorporation, filler dispersion, better mould flow, better extrusion characteristics, enhancement of polymer tack etc. to the rubber compounds.

1.1 Mechanism of Plasticisation

Many theories have been postulated to account for the plasticisation mechanism of the plasticisers. However no single theory can account for the entire aspect of the mechanism. Hence a combination of concepts from different theories are to be taken to explain the behaviour of a particular plasticiser/polymer combination. Eventhough the mechanism of plasticisation is not yet completely understood, two theories have been advanced to account for the phenomenon. They are the lubricity theory[3,4] and gel theory.[5,6] According to the lubricity theory the resistance to deformation of polymer is mainly due to intermolecular friction of the polymer molecules and the plasticiser acts as a lubricant to facilitate movement of resin macromolecules over each other, thus reducing the internal resistance to deformation. In short the addition of a plasticiser to a plastic compound imparts pliability and distensibility into a plastic compound. The gel theory considers that rigidity of an unplasticised resinous mass is mainly due to an internal three-dimensional honeycomb structure or gel formed by loose attachments between resin macromolecules. According to this theory plasticisation is manifested essentially through solvent action. To be effective a plasticiser is required to have a solubility parameter close to that of the polymer, such that the two would be largely compatible. Both polar interaction and interactions through hydrogen bonding between the plasticiser molecules and polymer segments will explain plasticisation effect. One of the important aspects of the addition of plasticisers to high polymers is that each molecule of plasticiser carries with it a substantial increment of free volume. Free volume is defined by Doolittle[7,8], as the volume increase from the supercooled state at 0^0K to the liquid state at the temperature at which viscosity-measurements are made. It is now well known that the free volume of liquids is very important in regard to the ease with which flow takes place. The important concept is that smaller the plasticiser molecule, larger is the proportion of the total volume carry along with them. It is also noted that introduction of plasticiser molecules with a high polymer increases the fractional free volume in the blend over that of the polymer alone.[7]

Compatibility and efficiency are the two main factors that are to be considered while selecting a plasticiser for a particular polymer. Besides this, staining characteristics, performance, low temperature flexibility, effect on vulcanisation, ageing characteristics, molecular weight, chemical structure, cost etc. are also to be considered before selecting a plasticiser. Compatibility denotes to what extent a given plasticiser be able to form a stable compound with the polymer, while efficiency denotes the properties of the plasticiser needed to achieve the required level of the modification of a specific property. One of the main technical limitations of any externally plasticised composition is the potential loss of the plasticiser by migration under service conditions. Sometimes incompatibility of the plasticiser/polymer system leads to sweating or "blooming" of the plasticiser molecules. This not only alters the properties of the composition but, can have profound influence on health, safety and environment aspects (HSE) also. In the polymer industry this problem is tackled mainly by three approaches, by selection of suitable plasticiser type, by use of chemically reactive or polymerisable plasticiser and by surface treatment of the fabricated product so as to give an impregnable skin without modifying its bulk properties.

Certain polymers like polyethylene having crystalline structure are found to be difficult to transform into plasticised compounds as resistance to plasticisation is characteristic behaviour of crystalline polymers. On the other hand polystyrene shows behaviour typical of an amorphous polymer and accept unlimited amounts of plasticiser. In the case of PVC, addition of increasing levels of plasticiser does not destroy its ability to recover from mechanical deformation due to the fact that plasticised PVC retains its structural elements which constrain chain separation. It is the amorphous region in the polymer which accept the plasticiser while the ordered crystallites preserve the structure. In plasticised rubber compounds the constraints to chain separation are provided by permanent covalent crosslinking. In PVC it has been shown by X-ray diffraction studies that addition of low levels of plasticiser results in embrittlement of the polymer known as antiplasticisation. This may be due to the increase in crystallinity of the polymer by lowering the energy barrier to rearrangement of the polymer chains within amorphous regions so as to give an ordered structure.[9]

In the conventional compounding of rubber, besides rubber, it involves sulphur, activator, accelerator, filler, processing aid etc. The main function of the processing aid or physical plasticiser, is to modify the physical properties of either the compounded rubber or the finished vulcanisate. The material used as processing aid must be completely compatible with the rubber and the compounding ingredients. Petroleum based process oils viz. aromatic, naphthenic and paraffin oils are generally used in the rubber as process aids and extenders. Generally rubbers can broadly be classified into polar and nonpolar depending on the nature of the constituent monomer. Nitrile rubber (NBR) is highly polar while natural rubber (NR), synthetic isoprene rubber (IR), polybutadiene (BR), styrene butadiene(SBR) etc. are non polar. Polychloroprene(CR) has got intermediate polarity. Petroleum based process oils are also classified according to their viscosity gravity constant (V.G.C) values. A high V.G.C. oil stands for high aromaticity and have greater polarity. For polar rubbers polar plasticisers are generally preferred while for non-polar rubbers various grades of mineral oils with low V.G.C. values are preferred based on their compatibility. Processing aids usually cause reduction in viscosity of the compounded rubber, facilitate filler incorporation, reduce power consumption and minimise scorch by reducing internal friction during processing operations like calendaring and extrusion. It is a well known fact that the segmental motions of polymer chains in cured rubber is much dependent on the concentration of crosslinks in the vulcanisate. Less crosslinked rubbers show more segmental frequencies and higher heat build up. Plasticiser addition usually makes compound to soften and reduce the friction between the polymer chains and hence increased segmental frequencies and heat build up. Milling action usually produces low molecular weight fragments which make the mass more plastic and less elastic. Busse and Cotton[10,11] in their study found that molecular breakdown during mastication is both a function of molecular oxygen and temperature. It is now common practice in rubber industry to use chemicals like pentachlorothiophenol, phenyl hydrazine etc. as chemical plasticisers to speed up molecular breakdown during mastication. From the work of Pike and Watson[12], now it seems certain that for chemical plasticisers to be effective, they must be radical acceptors and oxidation catalysts.

In order to achieve the best dispersion of fillers in the shortest possible time, it is common practice to add other ingredients after the initial breakdown of the rubber. This procedure prevents reduction of the viscosity of the rubber and hence effect shearing and breakdown of agglomerates which is a precondition to achieve good dispersions. However a penalty is paid for this in the form of heat generation and higher power consumption. In addition to the use of processing aids in the primary mixing operation, they are also beneficial in subsequent operations like, to sheet out stock smoothly from warm up mills, to extrude smoothly and with a minimum dimensional change in tubing operations, to maintain gauge in calendaring and skin coating of fabrics.

1.2 Vegetable oils as process aid

Utilisation of vegetable oils and chemically modified oils in place of conventional plasticisers assumes special role in the plasticiser technology as these oils are available in nature and are comparatively cheap, also there are reports of toxicity of some conventional process aids while the natural oils are non toxic in nature.[13] Use of vegetable oils in rubber compounding has been reported earlier.[14] Certain unsaturated oils such as linseed, rapeseed, and safflower oils were tried in neoprene rubber to improve properties like low temperature flexibility and tear resistance. The use of vegetable oil as crosslinking agent has also been reported.[15] Vegetable oils are used for producing factice by treating with sulphur. The brown factice from vegetable oils is reported to be suitable for improvement in properties of rubber mixtures and vulcanisates. The effect of factice, prepared from hydrogenated soya oil on the physical and mechanical properties of vulcanised NR, SBR, and CR were reported.[16] It was found that factice improved the after ageing properties of natural rubber vulcanisates.

1.3 Rice bran oil (RBO)

Rice bran oil (RBO) is available at very low cost in India. The oil is extracted from rice bran, which in turn is a byproduct of the rice milling process. Fatty acids are the most important constituents of oils and fats. In rice bran oil, palmitic, oleic and linoleic acids constitute the major three fatty acids present, followed by myristic, palmitoleic, stearic, linolenic and arachidic acids as the minor components. The fresh bran contains 1.4% to 1.9% free fatty acids (FFA).[17] On storage the FFA content may reach upto 30% within 10 days.[18] This may be attributed to the presence of an active enzyme called lipase in the bran. This enzyme catalyses the hydrolysis of lipids into fatty acids. The high FFA content of the oil extracted from stored rice bran may be prevented by stabilisation of the rice bran by acid or heat. In fact it is reported that acid and heat stabilisation are equally effective for the control of FFA[19]. Bhattacharya et. al. in their study reported that RBO of 15 to 30% FFA could be deacidified to low levels by re-esterification with glycerol after degumming and dewaxing[20]. After refining, bleaching and deodorization, the resulting low FFA oil may be utilised for cooking purposes.[21,22] This oil can also be used as a pan-release agent in the baking industry, brominated to an essential oil stabilizer and soft drink clarifier or sulphonated to emulsifiers, wetting and dispersing agents. Dewaxed crude rice bran oil, by cooling to 17°C and then centrifuged, is reported to be tried as an antifoaming agent. It may also be used to break and control the foam formation in phosphoric acid production unit. [23]

The composition of the fatty acids of rice bran oil is given in the table below.

Table 1.1 Fatty acid composition of rice bran oil[24-27]

Constituent	Percentage of total FFA
Saturated	
Myristic	0.4 – 1
Palmitic	12 - 18
Stearic	1 - 3
Unsaturated	
Oleic	40 – 50
Linoleic	29 – 42
Linoleinic	traces – 1
Palmitoleic	0.2 – 0.4

It has been shown that the variety of rice influences the amount of oil obtained but the fatty acids of the oil had more or less the same general composition.[28] It has been indicated that the oil from bran-polish and from milled rice extracted with petroleum ether have similar fatty acid composition.[29] However, milled rice oil extracted with chloroform and methanol has a higher linoleic acid content and lower oleic acid than oil extracted with petroleum ether. The presence of phospholipids including phosphatidyl ethanolamine, phosphatidylcholine and phosphatidylinositol has also been demonstrated in rice bran oil. The fatty acids of phospholipids include linoleic 45.18%, oleic 34.02% palmitic 16.62% stearic 1.82%, plamitoleic 1.54% and myristic 0.82%.[30] Other than fatty acids, there are some unsaponifiable components in the rice bran oil. The unsaponifiable fraction of this oil, which is rather high in comparison with other edible oils, contains ferulic acid esters of triterpenoid alcohols, tocopherols, squalene and the naphthalene group of hydrocarbons.[31] A mixture of two or more ferulic acid esters of triterpene alcohol is called oryzanol and it is reported to have antioxidant property.[32] It has also been reported that RBO has cholestrol lowering ability, and this feature of the oil is attributed to the presence of oryzanol and some other components of the unsaponifiable matter present in the oil.[33,34]. Chan et. al.[35] have suggested a method for separating oryzanol from RBO, first by extracting the oil with alkaline methanol followed by heating the filtered extract to 39°C. A 20% citrate solution was then added to the extract and oryzanol was recovered. The percentage of unsaponifiable matter in RBO varies between 3.9 to 6.6%.[36,37] This oil also contains considerable amount of wax ranging from 2 to 6%.[38] The presence of chlorophyll often gives the oil a greenish shade. The characteristic odour of RBO is due to ferulates and squalene and its brown colour is attributed to methyl ferulates.

The amount of tocopherol in RBO ranges from 0.03 to 0.1%.[39] Tocopherols are potent antioxidants and the antioxidant property depends upon the presence of a free phenolic hydroxyl group. Chemically, they are chroman derivatives.[40] The shelf life of crude rice bran oil is found to be longer than that of the refined rice bran oil. This is attributed to the presence of significant amount of tocopherols having the potential to prevent the atmospheric oxidation and rancidity of the oil compared to the refined variety. The antioxidant role of α-tocopherol in the rancidity of oils like olive oil, sunflower oil etc. has been established.[41] It is also reported that incorporation of tocopherols in the level of 0.05-0.1% into polypropylene as antioxidant improved the heat stability of polypropylene food packaging materials at ≤ 150°C.[42]

1.4 Rubber compounding and vulcanisation

The word vulcanisation comes from "vulcan", the Roman God of fire and metal working. Vulcanistion is the technique of transforming rubber, from a plastic substance of very low strength and breaking elongation, to a resilient highly elastic material of considerable strength. During vulcanisation rubber is crosslinked and thereby the plastic material is converted into elastic rubber. Successful rubber technology depends largely on the ability to control the vulcanisation process.

Vulcanisation using sulphur was discovered by Goodyear, in the USA in 1839 and by Hancock in the UK at about the same time.[43] Vulcanisation by sulphur alone is very slow and time consuming process which often gives rise to vulcanisates of very low physical and mechanical properties and poor ageing characteristics. In order that the vulcanisation process might have practical industrial application it was necessary to find means of speeding up the reaction of sulphur with rubber. Oenslager[44] has shown that small amounts of aniline added to a rubber/sulphur formulation can enhance the rate of vulcanistion significantly. Later discoveries showed that a wide variety of amines can function in the same way.[45] These chemicals are called accelerators of vulcanisation. Generally these organic accelerators do not function at their best without other assisting chemicals known as activators. These activators are usually metal oxides such as lead oxide, zinc oxide, magnesium oxide etc, and fatty acids such as lauric, stearic. Vulcanisation proceeds through a sequence of complex reactions which are not yet completely identified and understood. During crosslinking of rubber with sulphur the latter gets chemically bound with the rubber network in different ways. The presence of monosulphide or polysulphide sulphur crosslinks between polymer chains have been established. In addition to these types of crosslinks, pendent polysulphide or cyclic monosulphide and disulphide linkages are also formed. The structural features of the vulcanisate network may be shown schematically as show in Fig.1.1.

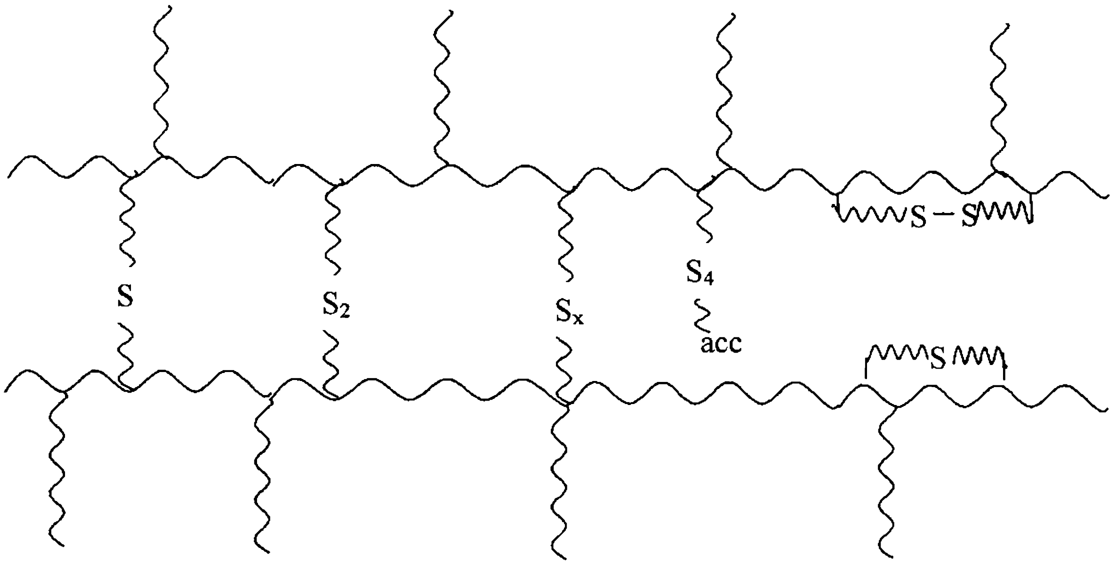

Fig. 1.1 Schematic representation of a vulcanised network formed during accelerator sulphur vulcanisation of rubber.

Vulcanization brings about a number of changes to the rubbers concerned. It increases retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus it increases elasticity while reducing plasticity. The retractile force to resist a deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer.

Binary accelerator systems are being widely used in the rubber industry as no single accelerator is found to be absolutely safe at processing temperature and which cures sufficiently fast. Apart from the synergism involved, the mechanism of acceleration by a binary system is not fully understood even now. The use of a novel binary accelerator system containing substituted dithiobiurets and tetramethyl thiuram disulphide/N-cyclohexyl-2-benzthiazyl sulphenamide (TMTD/CBS) in the sulphur vulcanisation of natural and styrene butadiene rubbers has been thoroughly investigated in this laboratory.[46,47] In this study it was found that the substituted dithiobiurets act as better nucleophiles and this fact was evidenced by the significant reduction in cure time values compared to the control mixes prepared with single accelerator.

Depending upon the accelerator sulphur ratio, the vulcanisation systems may be classified generally into the conventional or high sulphur vulcanisation system, the efficient vulcanisation (EV) system and the semi EV system.[48] In the conventional system sulphur is added in the range of 2.0-3.5 phr whereas the accelerator is added in the range of 1.0-0.4 phr. In this system sulphur is said to be inefficiently crosslinked. In the EV system sulphur is added in the range of 0.3-0.8phr and accelerator in the range of *6.0-2.5* phr . In this case the initial network is constituted of significant proportions of stable monosulphide crosslinks. Semi-efficient curing is effected by using sulphur in the range of 1.0-1.8 phr and accelerator in the range of 2.5-1.0 phr. As mentioned elsewhere in this chapter processing aids generally do not chemically react with the polymer and hence do not directly take part in the vulcanisation process. However certain compounds present in processing aids of hydrocarbon origin are found to assist vulcanisation reaction.

Hydrocarbons, the main component of petroleum based process aids, have negligible effect on the rate of cure. However certain compounds like high molecular weight heterocyclic aromatic compounds, naphthenic acid, phenols and certain basic constituents present in the aromatic oil do assist in vulcanisation reaction.[49,50]

1.5 Polymer blends

Blends of polymers are employed in product manufacture for a variety of reasons which include improved physical properties, increased service life, easier processing and reduced product cost. In polymer blends the property P depends on average proportion of the constituents and can be described by the following equation:

$$P = P_1 C_1 + P_2 C_2 + I P_1 P_2$$

Where P is the property of the blends, P_1 and P_2 are the properties of the individual components and C_1 and C_2 are the respective concentration of the compounds. I is the interaction parameter which can be positive, zero or negative as shown in the Fig. 1.2. When I is positive the property is synergistic, when I is zero the property is additive and when I is negative the property is non-synergistic. Blends are generally classified into two, miscible or homogenous blends and immiscible or heterogeneous blends. A homogeneous polymer blend will have one Tg value in between those of the two constituent polymers whereas a heterogeneous blend will have two values in between that of the constituent polymers. The mechanical properties of most of the heterogeneous rubber blends are found to be inferior to that of the constituent rubbers, mainly due to the 3 types of

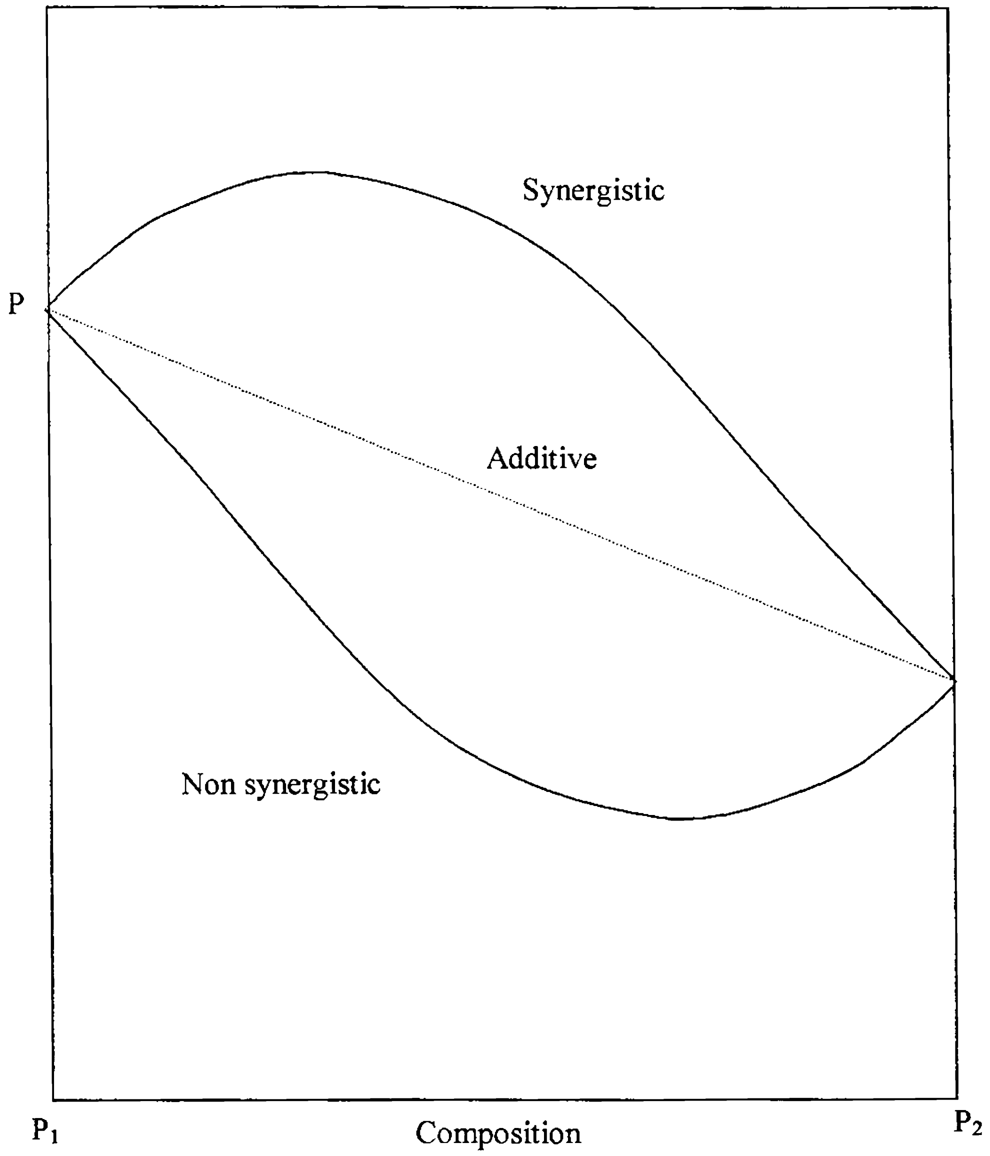

Figure 1.2 Variation of property with composition for a binary polymer blend

incompatibilities viz., thermodynamic incompatibility, viscosity mismatch and cure rate mismatch.[51] The thermodynamic incompatibility of polymer blends is governed by well-known Gibbs free energy relation

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the change in free energy of mixing, ΔH the change in enthalpy of mixing, ΔS is the change in entropy of mixing and T the absolute temperature. The thermodynamic incompatibility prevents mixing on a molecular scale.[52]

The majority of polymer blends are heterogeneous and exhibit a two phase morphology. When carbon black is added to a compound, it may not necessarily have the same affinity for each polymer. The uneven carbon black distribution may have significant effect on physical properties. The compound may consist of a highly filled phase blended with an unfilled, poorly reinforced phase.[53] The performance characteristics of an elastomer blend are frequently predictable from the ratio of the respective polymer components. In some instances, however, blends can be compounded to perform at a higher level for a particular property than would be anticipated from relative proportions of the individual elastomers. Examples of such behaviour are the increased electrical conductivity for very heterogeneous blends such as NR and CR.[54]

1.6 The scope and objectives of the present study

In the first part of the study we probed the effectiveness of rice bran oil as a multipurpose compounding ingredient for nitrile (NBR) and chloroprene (CR) rubbers. This oil has already been successfully employed in the compounding of NR and SBR in this laboratory. [55,56] In this context we thought it worthwhile to try this oil in the polar rubbers viz, NBR and CR also. The principle of like dissolves like as applicable to solvents is equally applicable while selecting a plasticiser, elastomer combination. Because of the compatibility considerations polar plasticisers are preferred for polar rubbers like NBR and CR. Although plasticisation is a physical phenomenon and no chemical reaction is involved, the chemical structure of plasticisers determines how much physical attraction there is between the rubber and the plasticiser. In this context it is interesting to note that the various fatty acids present in rice bran oil have a long paraffinic chain, characteristic of waxes, with an acid group at the end of the molecule. The paraffinic end of the molecule contributes lubricating effects and limits compatibility whereas the acid end group contributes some polarity and is also chemically reactive. Because of absorption of acid group on the surface of pigments, these acids will have active pigment wetting characteristics also. These factors justifies the role of rice bran oil as a co-activator and lubricating agent for NBR and CR. In fact in our study we successfully replaced stearic acid as co-activator and aromatic oil/DOP as processing aid for CR and NBR with rice bran oil.

This part of the study has got special significance in the fact that rubber industry now heavily depends on petroleum industry for process oils. The conventional process oils like aromatic, naphthenic and paraffinic oils are increasingly becoming costlier, as its resources in nature are fast depleting. Moreover aromatic process oils are reported to be carcinogenic because of the presence of higher levels of polycyclic aromatic compounds in these oils.[13] As a result of these factors, a great amount research is going on world over for newer processing aids which are cost effective, nontoxic and performance wise at par with the conventional ones used in the rubber industry. Trials with vegetable oils in this direction is worth trying.

Antioxidants are usually added to the rubber compound to minimise ageing effects from heat, light, oxygen etc. As rice bran oil contains significant amount of tocopherols and oryzanol which are natural antioxidants, we replaced a phenolic antioxidant like styrenated phenol (SP) from the compound recipe of both the rubbers with RBO and ascertained whether this oil could function in the role of antioxidant as well.

Preparation and use of epoxidised rice bran oil as plasticiser has already been reported.[57] The crude rice bran oil having an iodine value of 92 was epoxidised in this laboratory using peracetic acid in presence of sulphuric acid as catalyst. The epoxy content of the epoxidised oil was determined volumetrically by treating a known weight of the oil with excess HCl and back titrating the residual HCl with standard alkali solution. The epoxidised oil having an epoxy content of 3.4% was tried in the compounding of NBR and CR as processing aids. And results of these investigations are also included in this chapter. In the second part of the study we tried how RBO/ERBO could perform when used as a processing aid in place of aromatic oil in the compounding of black filled NR-CR blends. Elastomers cannot have all the properties required for a particular applications, so it is common practice in rubber industry to blend two elastomers to have desired property for the resulting blend.[58] In this RBO/ERBO was tried as a processing aid for plasticisation, dispersion of fillers, and vulcanisation of black filled NR-CR blends.

Aromatic oil was used as a control. The results of our study indicate that these oils could function as a processing aid and when added together with carbon black function as a cure accelerator also.

PVC is compatible with nitrile rubber in all proportions, provided NBR has an acrylonitrile content of 25 to 40%. Lower or higher ACN content in NBR makes it incompatible with PVC.[59] PVC is usually blended with NBR at high temperatures. In order to reduce torque during mixing, additional amounts of plasticisers like DOP are added. The plasticiser should be compatible both with PVC and NBR so as to get a homogeneous blend. Epoxidised soyaben oil is reported to have been used in the compounding of PVC as it can perform both as an efficient plasticiser and heat stabilizer.[60] At present DOP constitute the largest consumed plasticiser in the PVC compounding. The migration of this plasticiser from food packaging materials made of PVC poses great health hazards as this is harmful to human body. In such a scenario we also thought it worthwhile to see whether DOP could be replaced by rice bran oil in the compounding of NBR-PVC blends Different blends of NBR-PVC were prepared with RBO and were vulcanized using sulphur and conventional accelerators. The various physical and mechanical properties of the vulcanisates were evaluated and compared with those prepared with DOP as the control plasticiser. Epoxidised rice bran oil was also tried as plasticiser for the preparation of NBR-PVC blends. A comparison of the processability and cure characteristics of the different blends prepared with DOP and ERBO showed that ERBO based blends have better processability and lower cure time values. However the elastographic maximum torque values are higher for the DOP based blends. Almost all of the physical properties evaluated are found to be slightly better for the DOP based blends over the ERBO based ones. However a notable feature of the ERBO based blends is the better percentage retention of elongation at break values after ageing over the DOP based blends. The results of these studies using rice bran oil and its epoxidised variety indicated that they could be used as efficient plasticisers in place of DOP and justifies their role as novel, nontoxic, and cheap plasticisers for NBR-PVC blends.

Chapter-wise description of the present study is as given below.

Chapter I	Presents a general account of plasticisers and processing aids. The characteristics of rice bran oil which makes it suitable as a processing aid is also included. A brief account on sulphur vulcanization and properties of polymer blends also form part of this chapter.
Chapter II	Explains the various experimental procedures adopted in the present study.
Chapter III	Results obtained on the use of RBO as a multipurpose compounding ingredient for NBR and CR are reported. The role of epoxidised rice bran oil in the compounding of these two rubbers is also included in this chapter.

Chapter IV	In this chapter the results obtained on the use of RBO as well as epoxidised RBO as processing aids for the black filled NR-CR blends at different blend ratio are reported.
Chapter V	This chapter explains the use of RBO as a novel plasticiser for NBR-PVC blends. Also included are results on the use of this oil in carbon black/silica filled NBR-PVC blends.
Chapter VI	The results on the use of epoxidised rice bran oil in NBR-PVC blends; both in the unfilled and filled systems.
Chapter VII	Is an overall summary and conclusions of the present study.

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CHAPTER II

Chapter II

EXPERIMENTAL TECHNIQUES

In this chapter a detailed description of the materials used and the experimental procedures adopted for the present investigations have been included.

2.1 Materials used

Natural Rubber (NR)

ISNR-5 used in this study was supplied by the Rubber Research Institute of India, Kottayam. It had the following specifications:

Dirt content, % by mass	0.05
Volatile matter, % by mass	1.00
Nitrogen, % by mass	0.70
Ash, % by mass	0.60
Initial plasticity, P_o	30.00
Plasticity retention index (PRI)	60.00

Chloroprene rubber (CR)

Chloroprene rubber used in this study was of W type with Mooney viscosity [ML(1+4) at 100°C] 47. The rubber was supplied by Du Pont, USA.

Acrylonitrile-butadiene rubber (NBR)

Nitrile rubber used in the study was Aparene N 854 NS supplied by Apar India, Mumbai, with acrylonitrile content 42% and Mooney viscosity [ML(1+4) at 100°C] of 55.

Poly(vinyl chloride) (PVC)

Suspension polymer in powder form with a K value of 65. The resin was supplied by IPCL, Vadodara, India.

Compounding ingredients

1. Zinc oxide (activator)

Zinc oxide supplied by M/s. Meta Zinc Ltd., Bombay of the following specifications was used:

Specific gravity ([illegible])	5.5
Zinc oxide content	98%
Acidity	0.4%
Loss on heating (2 hrs at 100°C)	0.5%

2. Magnesium oxide

Magnesium oxide (MgO) used in the study was of commercial grade calcined light magnesia with a specific gravity of 3.6, supplied by Central Drug House (P) Ltd., Mumbai.

3. Stearic acid (co-activator)

Stearic acid supplied by Godrej Soaps (Pvt.) Ltd., Bombay, and having the following specifications was used in the study.

Melting point (°C)	65
Acid number	200
Iodine number	9.05
Specific gravity ([illegible])	0.85
Ash (%)	0.1

4. Mercaptobenzthiazyl disulphide (MBTS) (Accelerator)

Mercaptobenzthiazyl disulphide was supplied by Bayer Chemicals, Bombay. It had the following specifications:

Specific gravity ([illegible])	1.34
Melting point (°C)	165

5. Tetramethyl thiuram disulphide (TMTD) (Accelerator)

TMTD was supplied by Polyolefins Industries Ltd., Bombay. It had the following specifications:

Melting point (°C)	138
Specific gravity ([illegible])	1.4
Ash (%)	0.5
Moisture (%)	1.0

6. 2-Morpholinothio benzothiazole (MOZ) (Accelerator)

Melting point (°C)	80
Specific gravity ([illegible])	1.36
Moisture (% by mass)	0.3
Ash (% by mass)	0.25

7. Ethylene thiourea (Na22) (Accelerator)

Ethylene thiourea was obtained from National Physical Oceanographic Laboratory, Cochin, India and was of commercial grade.

8. Sulphur (crosslinking agent)

Sulphur was obtained from Standard Chemical Company, Chennai. It had the following specifications:

Specific gravity	2.05
Acidity (%)	0.01
Solubility in CS_2 (%)	98

9. Styrenated phenol (SP)

Styrenated phenol used was supplied by Synthetics and Chemicals Ltd., Bareilly. It had the following specifications:

Relative density	1.08
Viscosity at 27°C (cps)	2000-6000

10. Fillers

High abrasion furnace black N-330 supplied by M/s.Carbon and Chemicals India Ltd., Cochin of the following specifications was used:

Appearance	Black granules
DBP absorption (cc/100g)	102± 5
Pour density (kg/ m^3)	376.0
Iodine number	82
Loss on heating (per hour at 125°C) max (%)	2.5

Precipitated silica (vulkasil-s) was of commercial grade and was supplied by Rubo Chem Industries, Kottayam. It had the following specifications:

pH (5% aq. solution)	6.3
Specific gravity ([illegible])	2.03
SiO$_2$ hydrate on dried samples (min.) (%)	90
Nitrogen free surface (m^2/gm)	175±15
Loss on heating (105°C, 2 hrs) (%)	5.5

11. Aromatic oil

Aromatic oil supplied by Hindustan Organic Chemicals, Cochin of the following specifications was used.

Specific gravity (g/cm^3)	0.98
Aniline point (°C)	43.00
Ash content (% by mass)	0.01
Viscosity gravity constant	0.96

12. Dioctyl phthalate (DOP)

DOP used was of commercial grade supplied by Rubo-Synth Impex Pvt. Ltd., Mumbai. It had the following specifications:

Specific gravity (g/cm^3)	0.986
Viscosity (cps)	60

13. Rice bran oil (RBO) used in the study was supplied by Tamil Nadu Agro Industries Corporation, Thanjavur. It had the following specifications:

Colour (Y+5R, 1 cm cell)	37
Moisture and volatile matter (% w/w)	0.8
Flash point (°C)	210
Free fatty acid (% as oleic acid)	6-58
Iodine value (wij's)	92
Unsaponifiable matter (% w/w)	4.2
Refractive index (40°C)	1.46
Phosphatides (% w/w)	1.8

Wax (% w/w)	3.5
Hydroxyl value	11
Chlorophyl content (ppm)	2

14. Other chemicals

Hydrogen peroxide, glacial acetic acid, concentrated sulphuric acid, sodium hydroxide, potassium hydroxide, phenolphthalein, ethylene glycol, were all of analytical grade.

Solvents

Solvents used in the study viz., toluene, benzene, methanol, ethanol, chloroform were all of analytical grade.

2.2 Experimental procedure

Study of the processability of the compounds and melt mixing of NBR-PVC blend using Brabender plasticorder

A Brabender plasticorder model PL 3S was used for comparing the processability of the various compounds prepared with rice bran oil with that of the compounds prepared with conventional process aids. This instrument manufactured by M/s.Brabender OHG Duisburg, Germany has been widely used for measuring processability of polymers, rheological properties of polymer melts, blending of polymers etc.[1-3]

The Brabender torque rheometer is essentially a device for measuring torque generated due to the resistance of a material during mastication or flow under pre-selected conditions of shear and temperature. A jacketed mixing chamber with a volume capacity of 40cc constitute the central part of the plasticorder. Mixing and shearing of the material in the mixing chamber is done by two horizontal rotors with protrusions. The resistance put up by the test material against rotating rotors in the mixing chamber is indicated with the help of a dynamometer balance. The dynamometer is attached to a mechanical measuring system which records the torque. A DC thyrister controlled drive is used for speed control of the rotors. The temperature can be varied up to 300°C. Stock temperature thermocouple with a recorder is used for temperature measurements. The materials are charged into the mixing chamber after setting the test conditions to obtain a torque time curve or a plastogram.

The nature of shear in the plasticorder is similar to that encountered in practical processing operations such as extrusion or milling. Blyler and Daane[4] observed that the power law relationship between rotor torque and rotor speed is reminiscent of the power law relationship often found between shear stress and shear rate, and with a few assumptions derived the equation,

$$M = C(n)\ KS^n$$

where M is the torque

n, the power law index

$C_{(n)}$, a function weakly dependent on ‘n’

K, a constant

S, the rotor speed.

The slope of the plot of $\log M$ vs. log s gives the power law index. Also torque/rpm of the Brabender plasticorder represents viscosity and the activation energy for viscous flow can be measured from it if log (torque/rpm) is plotted against 1/T. The activation energy at constant rpm obtained by this procedure should correspond to the flow activation energy at constant shear rate.

In the present study, the processability of nitrile and chloroprene (CR) rubber compounds and NR-CR and NBR-PVC blend compounds prepared using rice bran oil (RBO) and epoxidised rice bran oil (ERBO) were compared with those of the corresponding compounds prepared with conventional processing aids using a Brabender plasticorder. In the case of NBR and CR the rubber was first masticated for 2 minutes at 40 rpm in the plasticorder with rotor mixing heads at room temperature (27°C). Activator and co-activator were then added within 2-3 minutes. Carbon black mixed with RBO/ERBO/conventional processing aids was then added followed by sulphur and accelerator. The total mixing time was kept at 16 minutes. In the case of NBR-PVC blend the temperature of the rotor mixing head was kept at 150°C. NBR was first masticated for 2 minutes. PVC resin mixed with heat stabilisers and DOP/RBO/ERBO was then added so as to get a uniform mix. The total mixing time was kept below 8 minutes. The experiment was repeated at different rpms. The flow curves were drawn by plotting torque/rpm against rpm.

Blending of NBR with PVC was also done in a similar sequence as mentioned above. The basic principle followed was to ensure the melting of polymers and to keep polymer degradation to minimum.

2.3 Mixing and homogenisation of the rubber compounds

Mixing and homogenisation of elastomers and compounding ingredients was done on a laboratory size (6"x12") two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002x100)". Then it was given two passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 60±5°C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per sequence given in ASTM D 3182-89. Before the addition of accelerators and sulphur the batch was thoroughly cooled. After completion of the mixing, the compound was homogenised by passing six times endwise through a tight nip and finally sheeted out at nip gap of 3 mm. Mixing time and temperature were controlled during the process.

2.4 Determination of cure characteristics

The cure characteristics of the mixes were determined using a Goettfert elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle (±0.2°). The frequency is 50 oscillations per minute. The torque is measured on the

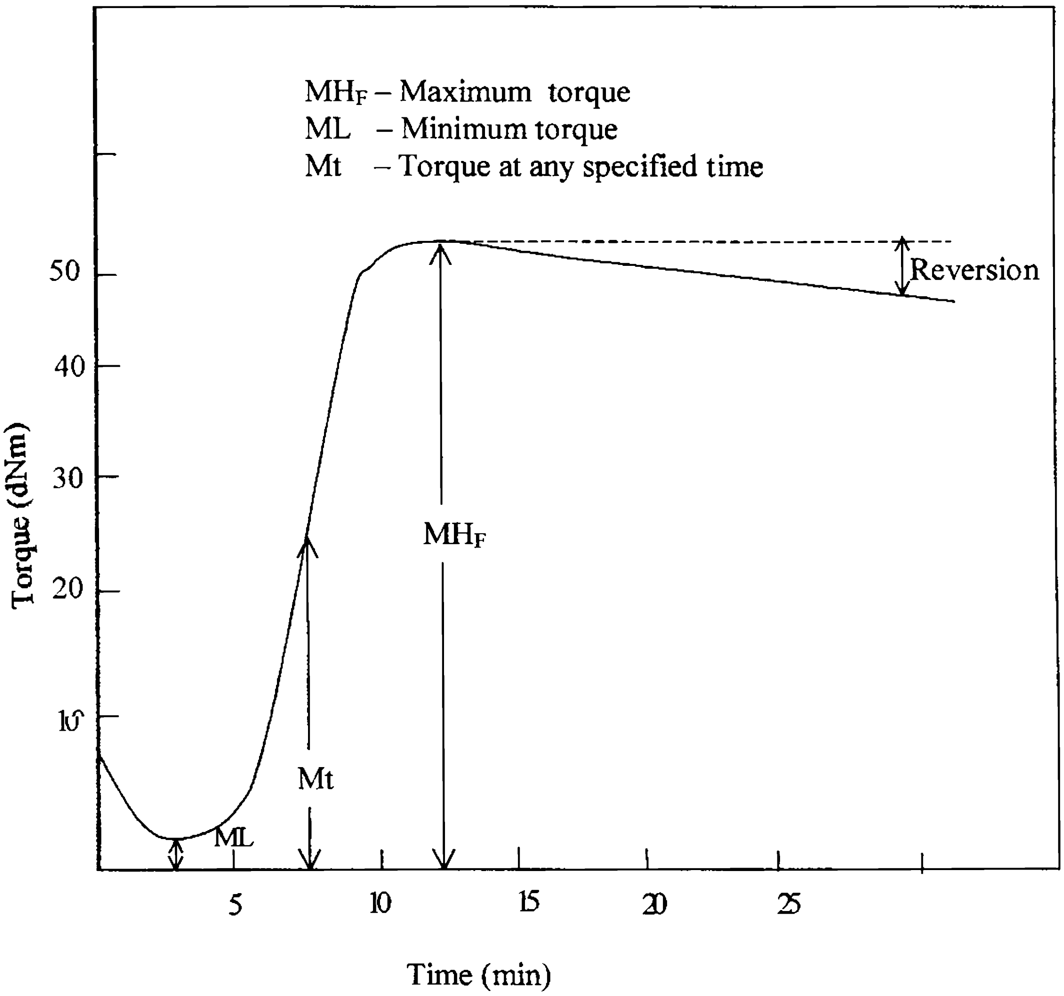

Fig. 2.1 Analysis of a typical cure curve to find out various cure parameters of a rubber mix

lower oscillating die half. The following data can be obtained from a typical elastograph cure curve as is shown in Fig.2.1

1. Minimum torque: Torque obtained by the mix after homogenising at the test temperature before the onset of cure.

2. Maximum torque: This is the torque recorded after the curing of the mix is completed.
3. Scorch time (t_{10}). This is the time for attaining 10% of the maximum torque.
4. Optimum cure time (t_{90}): This is the time taken for attaining 90% of the maximum torque.
5. Cure rate index: This is calculated as $100/t_{90}-t_{10}$ where t_{90} and t_{10} are the times corresponding to optimum cure and scorch respectively.

2.5 Moulding of test specimens

The test specimens for determining the physical properties were moulded in standard moulds by compression moulding in an electrically heated hydraulic press having 30x30 cm platens at a pressure of 11.764 MPa on the mould. The rubber compounds were vulcanised upto their respective optimum cure times and at specified temperatures. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

2.6 Physical test methods

Physical test on vulcanisate properties such as tensile strength, hardness, abrasion resistance, tear, compression set, crack growth etc. have been standardised in the rubber industry to design compounds to meet service conditions, to investigate product or process failures and to ascertain quality assurance for a quicker prediction of quality. The most commonly sought physical property of any rubber vulcanisate is its tensile strength and it is defined as the force on unit area of original cross section which is required to break the test specimen, the condition being such that the stress is substantially uniform over the whole of the cross section. The elongation at break [EB] is the maximum value of the elongation expressed as a percentage of the original length. The value of tensile stress (force/unit area) required to stretch the test piece from the unstrained condition to a given elongation is called modulus or more accurately "tensile stress at a given strain". Physical properties can differ lengthwise and cross-section wise on a section of rubber compound due to anisotropy. Dumb-bell shaped test specimens are used for tensile strength value determination. The dumb-bell shaped test specimen take into account the main problems in tensile testing. First, the difficulty of holding the rubber securely without any slipping and secondly to avoid the high local stresses in the test piece which would cause premature rupture at the grips.

Tensile strength in itself bears little relation to product service, as rubber is not normally used at such high elongations that there is a danger of failure due to tensile rupture even after moderate heating. Though tensile strength has got very little significance as a service test, it is extremely useful for many comparison studies. High tensile strength coupled with a reasonable EB can only be obtained with high quality rubber mixes and for this reason tensile strength is very often included in specifications. They are also useful for determining the curing characteristics of compounds. The cure condition giving the highest tensile strength being widely adopted as optimum cure. Deterioration of rubber on ageing can be followed by the drop in tensile strength. Effect of many compounding ingredients as well as that of pigment dispersion can be decided by tensile strength tests. Finally, as a control test, it is invaluable since any mistake in mixing or processing giving inferior product is indicated by a drop in tensile strength. For parameters described below, atleast three specimens per sample were tested for each property and the mean values are reported.

a) Tensile stress-strain properties

Tensile properties of the vulcanisates were determined as per ASTM D 412 (1987) using dumb-bell specimens on a Zwick universal testing machine (model 1445). All the tests were carried out at 28±2°C. Samples were punched out from compression moulded sheets using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held by the two grips on the UTM, the upper grip of it was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. The tensile strength, elongation at break and modulus were printed out after each measurement by the microprocessor.

b) Tear resistance

This test was carried out as per ASTM D 624 (1986) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on the Zwick Universal testing machine. The speed of extension was 500 mm/min. and the test temperature 28±2°C.

c) Hardness

The hardness (shore A) of the moulded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1986). The tests were performed on unstressed samples of 30 mm diameter and 6 mm thickness. A load of 12.5 N was supplied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimen.

d) Compression set

The samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set (\%)} = \frac{t_o - t_1 x 100}{t_o - t_s}$$

where t_o and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used. The procedure adopted was ASTM D 395 (1986) (Method B).

e) Abrasion resistance

The abrasion resistance of the samples was determined using DIN abrader (DIN 53516). Cylindrical samples having a diameter of 15mm and length 20mm was kept on a rotating sample holder and 10N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece abraded by its travel through 42M on a standard abrasive surface. The abrasion loss was calculated as follows:

$$V = \frac{\Delta M}{\rho}$$

where ΔM = mass loss per hr ρ = density of the sample, V = abrasion loss.

The result is expressed in cm^3/hr.

f) Ageing studies

Ageing studies were carried out according to ASTM D 573-88. Dumb-bell samples were kept in an air oven at 100°C for 72 hrs in the case of NBR and for 96 hours in the case of CR rubber. For NR-CR blend the ageing was done at 100°C for 24 hours and for NBR-PVC blend, the sample specimens were aged for 96 hours. Physical properties like tensile strength, elongation at break, modulus etc. were measured after ageing. Knowing the values of these tests before ageing, the retention of these properties was calculated for assessing the effect of ageing.

g) Density

Density of the samples was determined as per ASTM D 297 (1981). In this method the weight of the specimen in air was first noted and then specimen was immersed in water and its loss of weight in water was determined. The density is given by

$$\frac{\text{Weight of specimen in air } \mathbf{X} \text{ density of water}}{\text{Loss of weight of specimen in water}}$$

2.7 Chemical test method

Estimation of free fatty acids in rice bran oil[5]

Neutralised ethyl alcohol was first prepared by adding dilute sodium hydroxide solution to the alcohol using 3 drops of phenolphthalein as indicator until a pale pink colour persist. A known weight of RBO was weighed into a conical flask, to which 50 ml of neutralized alcohol was added and boiled in a water bath for 5 minutes. This hot solution was then titrated against 0.1N sodium hydroxide until the pale pink colour was restored. The free fatty acid in the oil is expressed in terms of oleic acid as it constitutes the major component in the oil. Based on the above titre value, the free fatty acid was calculated.

Preparation of epoxidised rice bran oil

In a typical experiment, 25 grams of crude rice bran oil [(1.V = 92; 0.091 moles of double bond] 6 grams of benzene, 2.73 grams of acetic acid (0.5 mole/mole of double bond in oil) and sulphuric acid (2% total weight of hydrogen peroxide and acetic acid added as 1:1 acid) were mixed under stirring in a three necked flask, provided with a thermometer and a condenser. 30% hydrogen peroxide (15.47 gms, 1.5 mole/mole of double bond in oil) was added slowly over a period of 2 hours and the temperature was maintained at 60-65°C for 14 hours. The expoxidised oil was isolated.[6] and vacuum dried. The products were analysed for their oxirane oxygen and iodine value.[7]

Determination of the iodine value of the oil

A known weight of the oil (0.2g) is weighed into an iodine flask and dissolved in 20ml CCl_4. This is then allowed to react with 10 ml of 0.1N of iodine monochloride (ICI) in CH_3COOH in presence of mercuric chloride (catalyst) in ethanol for one hour in darkness. After the reaction has been completed 10ml of 15% of KI solution and 50ml distilled water is added and titrated against standard thiosulphate solution using starch indicator. A blank experiment is also conducted. By knowing the volume of thiosulphate used for the two experiments the iodine value of the oil may be calculated using the equation

$$\text{Iodine value} = \frac{(B-V) \times N \times 126.9 \times 100}{1000 \times W}$$

where

B = Volume of thiosulphate used for blank

V = volume of thiosulphate used for sample

N = Normality of thiosulphate

W = Weight of sample taken.

Determination of oxirane oxygen[8]

Becauses of the strained three membered ring, α-epoxides are the most reactive of the expoxides and are more reactive than ethers. Thus they react with HCl to form corresponding chlorohydrins. A known weight of the epoxide is added to a measured volume of the reagent (HCl-dioxan) in excess and after the reaction is completed the residual HCl is determined by titrating against standard alkali. The difference between the amount of acid present before and after the reaction is taken as a measure of the α-epoxide content. The procedure employed is given below. 25 ml of HCl dioxan reagent was pipetted into a 50 ml iodine flask. About 0.5 gm of the epoxidised oil was weighed into the flask. The reaction mixture was allowed to stand for 15 minutes, 25 ml of neutral ethyl alcohol prepared by using 1 ml cresol red indicator was then added to the reaction mixture. The excess of the acid present in the mixture was titrated with standard 0.1N methanolic sodium hydroxide. The colour of the indicator changes from pink to yellow just before the end point and from yellow to violet at the end point. A blank titration was also conducted with 25 ml HCl-dioxan reagent only. The free acids in the sample was determined by dissolving a known weight of the sample in 50 ml neutral ethanol and then titrating against standard 0.1N methanolic sodium hydroxide. The volume of the standard alkali for the weight of epoxidised rice bran oil employed in epoxy determination was then calculated. The percentage of oxirane oxygen is thus given by the equation.

$$\text{Oxirane } O_2\ (\%) = \frac{V_1-(V_2-V_3) \times N_1 \times 16 \times 100}{W \times 1000}$$

V_1 = volume of NaOH used for blank

V_2 = volume of NaOH used for sample

V_3 = volume of NaOH used for titration of the free acid in the sample.

N_1 = Normality of the NaOH

W = Weight of the sample

Determination of chemical crosslinks of the vulcanisates

The crosslink density of the vulcanisates was determined from the equilibrium swelling data as follows.

Approximately about 0.2 gm of samples were cut and kept to swell in suitable solvents for 24 hours. The outer portion of the swollen samples was then dried using a filter paper and weighed. It was then placed inside the oven at 60°C for 24 hours to remove the solvent. The deswollen weight was determined. The volume fraction of rubber in the deswollen network was then calculated by the method reported by Ellis and Welding[9-11] from the following equation

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1} + A_o \rho_s^{-1}}$$

where T = weight of the test specimen; D = deswollen weight of the test specimen; F = weight fraction of insoluble component; A_o = weight of the absorbed solvent corrected for the swelling increment; ρ_r = density of test specimen; ρ_s = density of solvent.

In the case of vulcanisates containing filler the value of Vr obtained as above were converted into V_{ro}, by means of an equation derived by Porter

$$\frac{V_{ro}}{V_r} = 0.56e^{-z} + 0.44$$

where V_r is the volume fraction of rubber without the filler, z is the weight of the filler divided by total weight of all ingredients, and V_{ro} is the volume fraction of rubber with filler. This value was then substituted in the Flory Rehner equation (as reported in Chapter III) in place of V_r to obtain the crosslink density.

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CHAPTER III

Chapter III

THE COMPOUNDING OF NITRILE AND POLYCHLOROPRENE RUBBERS WITH RICE BRAN OIL/EPOXIDISED RICE BRAN OIL

Use of vegetable oils as processing aids is not unknown to rubber industry. In the present study an attempt is made to probe the effectiveness of rice bran oil (RBO) as a multipurpose compounding ingredient for the two polar rubbers viz., nitrile (NBR) and polychloroprene (CR). It has already been established that rubber mixes containing vegetable oils and vulcanized vegetable oils give better flow properties, plasticising action, low temperature flexibility and ozone resistance.[1,2] Vegetable oils like linseed oil is also reported to be tried as plasticiser in heat resistant neoprene rubber and in some elastomer blends for cold resistance.[3,4] This oil has also been used as a vulcanizing agent in carboxylated nitrile rubber ionomer blends.[5] Rape seed oil has also been found to be effective as processing aid for chloroprene rubber. It is also recorded that the factice w, prepared from hydrogenated soya oil improves the physical and mechanical properties of NR and CR vulcanisates, especially after ageing in air oven for 72 hours at 70°C.[6] It is reported that the RBO has got excellent compatibility with fluororubbers and the oil gives good extrusion moldability for the rubber.[7] Studies on use of vegetable oils as crosslinking agent has also been reported. It is found that the brown factice from vegetable oils is suitable for improvement of rubber mixtures and vulcanizates.[8]

Preparation of epoxidised rice bran oil and its use as a plasticiser has also been reported.[9] Epoxidation of RBO and its acetate and alkyl esters with H_2O_2 is also reported.[10] In the present study the epoxidised rice bran oil (ERBO) with an epoxy content of 3.4%, prepared by using per acetic acid, is employed in the compounding of nitrile and polychloroprene rubbers. The effectiveness of ERBO as a processing aid for these two polar rubbers was compared with that of the conventional processing aids (DOP/aromatic oil) employed for these rubbers.

In the conventional rubber compounding besides rubber it involves sulphur, activator, co-activator, accelerator, filler, processing aid etc. ZnO and stearic acid are the usual activator and co-activator used in the NBR curing system. Their function along with accelerator is to complete the vulcanization reaction in as short time as possible. It is a well known fact that processing aid causes reduction in viscosity of the compounded rubber, facilitate filler incorporation, reduce power consumption and minimize scorch by reducing internal friction during processing operations like calendaring and extrusion. Natural fats and oils like vegetable oils, blown oils, fatty acids etc. come under the category of physical softeners as they do not chemically react with polymer to which it has been incorporated. Instead these substances will act as intermolecular lubricants and perform a number of useful functions in the compounded stock such as increasing plasticity and workability, aiding incorporation of pigments reducing stickiness on the mill, providing lubrication to improve extrusion moulding, and reducing both temperature and power consumption during mixing. In some instances they will modify properties of the vulcanized stock. Besides these functions epoxidised rice bran oil is expected to give good ageing characteristics to the vulcanisate as this has got good thermal stability due to the presence of oxirane rings.

While selecting a particular plasticiser for a given rubber, the most important criterion to be considered is compatibility. A rule of thumb is that polar plasticiser is preferred for polar rubbers and the nonpolar plasticisers for the nonpolar rubbers. For the polar rubbers like NBR and CR polar plasticisers are preferred to improve processability and low temperature flexibility. The natural fats and oils are characterized by two opposing effects towards compatibility. A large portion of the molecule is made up of long paraffinic chains which are rather wax like in character and hence tend to give low compatibility towards polar polymers, but imparts good lubrication effect. At the same time in the same molecule there are ester groups which confer some degree of polarity and hence improve compatibility towards polar elastomers. In rice bran oil there exist a significant amount of free fatty acids and hence can exert the above mentioned two opposing effects towards compatibility due to the presence of long paraffinic chains and acid end groups. Besides this these acid groups can absorb on the surface of pigments. Thus this oil can be expected to have good pigment wetting characteristics. Above all these free fatty acids can also react with zinc oxide or basic accelerators so that they become a part of the vulcanizing system.

For NBR rubber ester or polymeric plasticisers are generally used because they not only influence processing but also affect properties such as hardness, low temperature flexibility and oil resistance. Small quantities of aromatic process oils can occasionally be used, especially with those types having less than 30% acrylonitrile (ACN) content. If high gum strength polymers which crystallize easily on stretching such as NR and CR are exposed to moderately low temperature for a considerable period of time, a time dependent reversible stiffening phenomenon known as crystallization occurs. For chloroprene rubber this is most rapid at 12°C. This crystallization may be minimized either by using very tight state of crosslinking or by compounding with increased amounts of filler and petroleum plasticisers including resinous type. In chloroprene rubber ester type plasticisers are generally avoided as they tend to increase crystallization rates, the reason for this is not fully understood. Thus plasticisers based on mineral oil are most often employed to improve processing of the polychloroprene mixes. Naphthenic oil is preferred provided the end product is not subject to hot air exposure. For improved flame resistance phosphoric acid esters or chlorinated hydrocarbons are generally employed. For higher loading aromatic mineral oil is used as it is more compatible with the rubber. However aromatic process oils are reported to be carcinogenic because of the presence of higher levels of polycyclic aromatic compounds in these type of oils.[11]

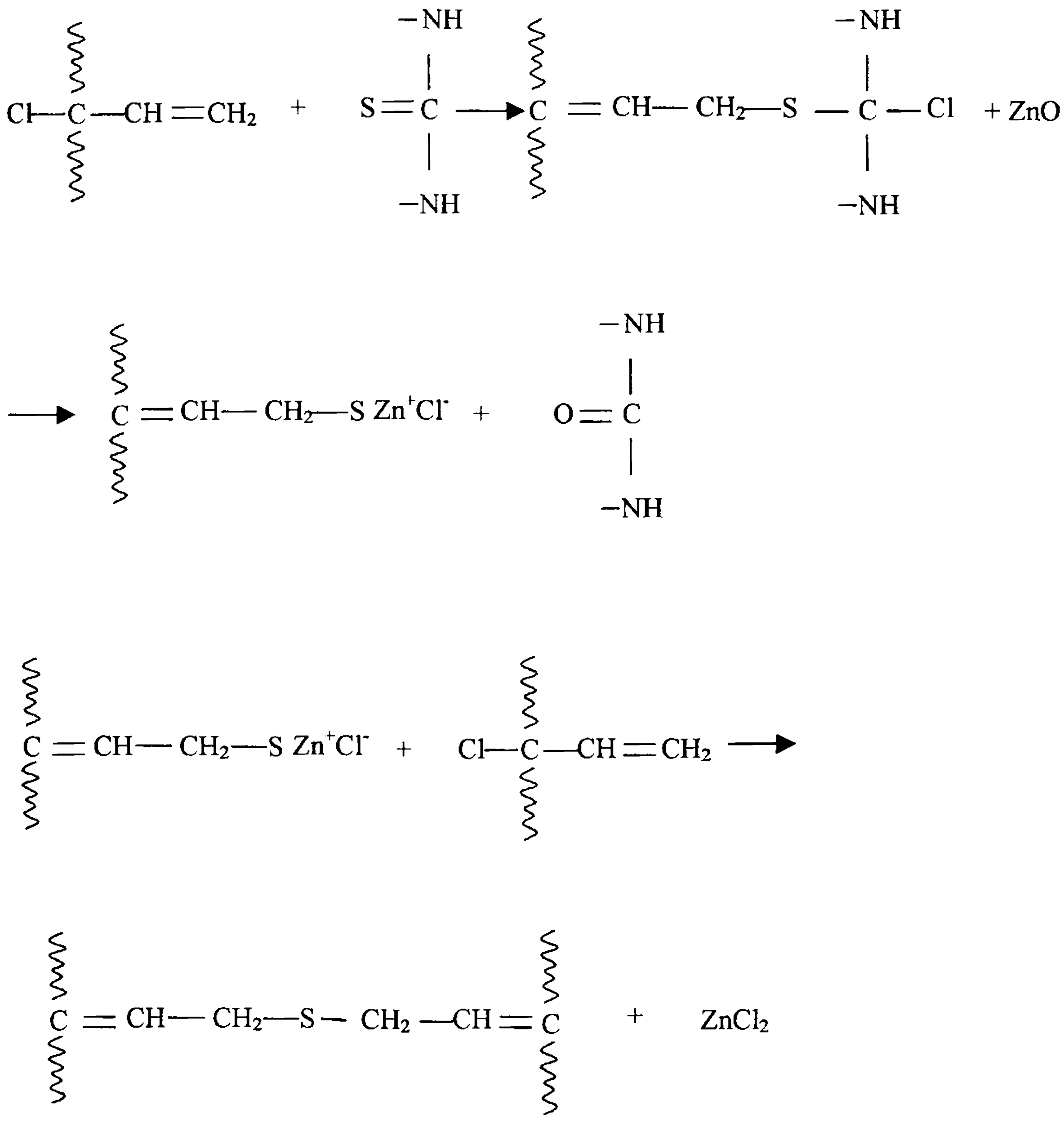
Antioxidants are added to the rubber compound to minimize ageing effects from heat, light, oxygen etc. Most of the active antioxidants are secondary aromatic amines. However, these materials turn dark upon exposure to air and light and hence not advised for using in light coloured compounds. Certain aromatic hindered phenols and its derivatives which have antioxidant activity and are non-discolouring have been used with success in light coloured compounds, eventhough they are not as powerful as the aromatic secondary amine type antioxidant. In rubber industry it is a common practice to use mixtures of antioxidants as no single antioxidant is found to be good enough against all types of ageing. Many commercial antioxidants are mixtures of one or more antioxidants chosen for their effectiveness against different types of ageing. Oxygen when combining with rubber causes two effects, namely chain scission and crosslinking. The chain scission manifest itself in tensile degradation and increased elongation while the crosslinking of the polymer manifest itself by stiffening as indicated by modulus increase and possibly hardness increase. It is the crosslinking effect that is commonly observed as a result of oxidation of chloroprene and nitrile rubbers. As a result of this elongation at break decreases and hardness increases but does not necessarily have a decreasing effect on tensile strength. A good antioxidant should have the following characteristics like, low melting point, easily dispersible in rubber, should not interfere in the vulcanization process, should not bloom in uncured or cured rubber, should have the general applicability and finally should be nontoxic.

A salient feature of the rice bran oil is that the oil contains significant amount of fatty acids, unsaponifiable matter, phosphatides and wax.[12] ** Nasirullah et al have obtained the following fatty acid composition for the crude RBO; myristic 1.2-3.3%, palmitic 18.0-20.3%, stearic 0.5-1% oleic 34-43.9%, linoleic 13-18%, linolenic 2.3-3.7%, from their gas chromatographic studies of RBO. The unsaponifiable[13] matter that comes from the glyceride portion of the oil consists of phytosterol, tocopherol, squalene, oryzanol and naphthene group of hydrocarbons. Phosphatides[14] mainly contain lecithin and is present to the order 0.6%. The role of tocopherol as an antioxidant[15] is well known as it inhibits the oxidation of unsaturated lipids by molecular oxygen.

** Ref: No 19 on Page 23.

In this context an attempt has been made to make use of the fatty acids and phenols in RBO as co-activator and antioxidant respectively. The formulations for the two rubbers under review were so selected that rice bran oil itself could be used instead of stearic acid as co-activator/lubricant and styrenated phenol as antioxidant.

A curing system based on sulphur, accelerator and activator is used for NBR. Here ZnO acts as the activator and stearic acid as the activator component. Because of the low solubility of the sulphur in the nitrile rubber sulphur is added during the initial stage of the mill mixing followed by other compounding ingredients. For chloroprene rubber a curing system based on metal oxides (ZnO/MgO) and Na22 (Ethylene thiourea) is used. The Na22 will act as an accelerator when used together with metal oxides. The function of MgO is to give maximum protection against scorch, so it is customary in mill mixing to add MgO first, followed by hard fillers, soft fillers, oils, lubricants with ZnO, and accelerator, if any, added in the final stage of mixing. The following curing mechanism may be postulated for chloroprene rubber when Na22 together with metal oxides is employed for vulcanization. In polychloroprene rubber 98% of polymer chain is built up through the 1-4 addition of the monomer unit. However, a small percentage of about 1.5% is built up by the 1-2 addition, and these are utilised in the vulcanization process as this arrangement leaves chlorine atom in both tertiary and allylic and hence strongly activated and thus becomes a curing site on the polymer chain. In CR, the double bonds are sufficiently deactivated by electronegative chlorine atom so that direct vulcanisation with sulphur is limited. But in the thiourea accelerated curing system the tertiary allylic chloride forms a complex which then reacts with ZnO and releases a molecule of urea. The residual zinc chloride mercpatide reacts with a second molecule of tertiary allylic chloride to form a sulphur bridge between the two polymer chains.[16] A schematic representation of the mechanism is as follows:



The role of metal oxides is an acid accepting function, ZnO being a promoter and MgO a retarder.

NBR being amorphous in nature needs fillers for reinforcement in order to have optimum physical properties. Both carbon black and non-black fillers are used with NBR. The tensile strength and tear resistance of polychloroprene gum vulcanisate are fairly good because of the strong tendency of the polymer to crystallize. However to acquire superior physical properties reinforcing or semireinforcing carbon blacks are used. Because of the presence of high molecular weight acids present in rice bran oil, it should function as a processing aid as well when used with filler in nitrile and polychloroprene rubbers. Besides this the oil could be used as a lubricant for chloroprene rubber instead of stearic acid, whose function is to reduce the friction between the polymer chains and thereby reduce temperature during the mixing operations. They also help to prevent the stock from sticking to the mill or calendar rolls.

In the present study the conventional processing aids, co-activator/lubricant and finally antioxidant used in the vulcanization systems of nitrile and chloroprene rubbers are effectively replaced with RBO. This is by virtue of the fact that this oil contains significant amount of free fatty acids, tocopherol and oryzanol. In order to assess the effectiveness of epoxidised rice bran oil as a processing aid in the black filled NBR and CR, we used different levels of this oil during compound preparation and the vulcanisate properties were then compared with the corresponding control mixes with DOP/aromatic oil.

EXPERIMENTAL

Nitrile and polychoroprene rubbers conforming to the specifications given in Chapter II was used in the present investigation. Zinc oxide, magnesium oxide, stearic acid, sulphur, mercapto benzothiazyldisulphide (MBTS), tetramethyl thiuram disulphide (TMTD), ethylene thiourea (Na22), styrenated phenol, carbon black (HAF 330), aromatic oil, and dioctyl phthalate (DOP) used are all of rubber grade. Rice bran oil obtained from Tamil Nadu Agro Industry Corporation, Thanjavur having free fatty acid content of 57.5% was used for the compounding of nitrile and chloroprene rubbers. For the preparation of epoxidised rice bran oil, RBO having a free fatty acid content 6% and iodine value of 92 was used. The experimental procedure for the determination of free fatty acid (FFA) and iodine value are detailed in chapter II. The crude rice bran oil was epoxidised by using hydrogen peroxide and glacial acetic acid in presence of sulphuric acid as catalyst. The experimental details are given in chapter II. The epoxide content of the ERBO is determined volumetrically by treating a known weight of the oil with excess HCl and back titrating the residual HCl with standard alkali solution. The details of the procedure is as given in chapter II. The epoxidised rice bran oil having an epoxy content of 3.4% is used for the present study.

Brabender plasticorder PL3S was used for comparing the processability of NBR and CR compounds with RBO/ERBO/DOP/aromatic oil. Mixes were prepared as detailed in Tables 3.1 and 3.2 except for the fact that different levels of RBO/ERBO/DOP/aromatic oil were used in the mix preparation. The processability of NBR using RBO/ERBO was compared with that of DOP. For CR the processability comparison was made between RBO/ERBO and aromatic oil. The torque rheometer is a device for measuring the torque generated due to the resistance of a material to mastication under the preselected conditions of shear and temperature. In the present study the materials are charged into the mixing chamber after setting the roller mixing heads at 40 rpm and at room temperature (27°C) to obtain a torque time curve or a plastogram. Nitrile or chloroprene was passed six times in a two roll mill at a nip gap of 0.8 mm to get a thin sheet. This was then cut into small strips before feeding into the plasticorder. The weight of the individual ingredients in the recipe of NBR or CR was so selected that the total weight of all the components in the recipe when put together comes below 40 gm. The total mixing time was 16 minutes with the following break-up. NBR or CR was masticated with 4 minutes followed by adding activators within 3 minutes. For NBR sulphur is added along with activators. Carbon black mixed with DOP/RBO/aromatic oil/ERBO was then added within 8 minutes and finally accelerators within one minute. The experiment was repeated by using 3, 5, 7 phr levels of DOP/RBO/ERBO for NBR and 2, 4, 6 phr levels of aromatic oil/RBO/ERBO for CR. In each case a Brabender torque-time curve (plastogram) was plotted for varying amounts of DOP/aromatic oil/RBO/ERBO.

After the mixing studies on the Brabender plasticorder the experimental mixes were prepared in a two roll mixing mill (6"x12") as per ASTM D 3182-89 at a friction ratio of 1:1.25 using the formulation given in Tables 3.1 and 3.2. Since the solubility of sulphur in NBR is poor, during mill mixing of the rubber sulphur is added in the beginning to ensure maximum solubility of sulphur. Reference mixes were prepared with DOP for NBR and with aromatic oil for CR. Mixes D_o, D_1, D_2, D_3 are based on NBR and DOP and C_o, C_1, C_2, C_3 are based on CR and aromatic oil. Apart from rubber filler and curing agent, mixes D_o and C_o contain both antioxidant and stearic acid. Mixes D_1 and C_1 contain no antioxidant, D_2 and C_2 contain no stearic acid and in D_3 and C_3 both stearic acid and antioxidant are replaced. R_0, R_1, R_2, R_3 and RC_0, RC_1, RC_2, RC_3 are the corresponding mixes prepared with rice bran oil. In order to assess the efficiency of ERBO as a processing aid for the black filled NBR rubber, different mixes were prepared using 3, 5 and 7 phr of ERBO. The corresponding mixes with DOP were also prepared. For CR different mixes with 2, 4, 6 phr of ERBO were prepared and their properties were compared to the ones prepared with 2, 4, 6 phr levels of aromatic oil.

The cure characteristics of the NBR and CR mixes were determined at 160°C and 150°C respectively, using Goettfert elastograph model 67.85. The cure properties obtained are reported in Tables 3.3 and 3.4. t_{90} is the optimum cure time (time to reach 90% of the maximum torque) and t_{10} is the scorch time (time to reach 10% of the maximum torque). The cure rate index is calculated as $100/t_{90}$-t_{10}. The compounds are vulcanized upto the optimum cure time in an electrically heated hydraulic press at 160°C/150°C at a pressure of 11.764 MPa. Tensile properties were determined as per ASTM D 412-87 using a Zwick-Universal testing machine at a pulling rate of 500 mm/min. at 27°C. Dumbell specimen for the test were punched out of the moulded sheets along the mill grain direction. Tear resistance was determined as per ASTM method D 624-86 using unnicked 90°C test pieces. Hardness was measured according to ASTM D 2240-86 and compression set according to ASTM D395-86 (Method B). Ageing studies were carried out as per ASTM D 573-88 at 100±1°C for 72 and 96 hours for NBR and CR vulcanisates, respectively, in an air oven.

Table 3.1 Formulation of NBR mixes

Ingredient	Mix No							
	D_0	D_1	D_2	D_3	R_0	R_1	R_2	R_3
NBR	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	0	0	2	2	0	0
Styrenated phenol	1	0	1	0	1	0	1	0
HAF black	40	40	40	40	40	40	40	40
DOP	5	5	5	5	0	0	0	0
RBO	0	0	0	0	5	5	5	5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 3.2 Formulation of CR mixes

Ingredient	Mix No							
	C_0	C_1	C_2	C_3	RC_0	RC_1	RC_2	RC_3
CR	100	100	100	100	100	100	100	100
MgO	4	4	4	4	4	4	4	4
ZnO	5	5	5	5	5	5	5	5
Stearic acid	0.5	0.5	0	0	0.5	0.5	0	0
Styrenated phenol	1	0	1	0	1	0	1	0
HAF black	40	40	40	40	40	40	40	40
Aromatic oil	4	4	4	4	0	0	0	0
RBO	0	0	0	0	4	4	4	4
Na 22	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

In order to understand the variation in physical properties of the different vulcanisates the density of crosslinks was also estimated. The Crosslink density of NBR vulcanisate was determined by equilibrium swelling in chloroform for 24h at 27°C. For CR the above experiment was carried out using benzene as the solvent. The total crosslink density is calculated using the Flory-Rehner equation

$$\tfrac{1}{2}M_c = -\frac{[\ln(1-\nu_{ro}) + \nu_{ro} + \chi \nu_{ro}^{2}]}{2\rho_r \nu_s (\nu_{ro})^{1/3}}$$

where ν_s = Molar volume of the solvent

χ = Interaction parameter characteristic of rubber and solvent

M_c = Number average molecular weight of the rubber chains between crosslinks.

The values of the interaction parameter taken for the calculation are the following:

NBR - chloroform, $\chi = 0.24$.

CR – benzene, $\chi = 0.26$.

The experimental details are given in Chapter II.

RESULTS AND DISCUSSIONS

Processability

The quantity of rice bran oil/epoxidised rice bran oil/DOP/aromatic oil required for the various compounds of NBR and CR was optimized using the Brabender plasticorder data. Figs. 3.1, 3.2 and 3.3 show the variation of Brabender torque with time of NBR compounds having 3, 5, 7 phr of DOP/RBO/ERBO. Figs. 3.4, 3.5, 3.6 show the torque values for CR compounds having different levels (2, 4, 6 phr) of aromatic oil/RBO/ERBO. As expected as the level of DOP/aromatic oil/RBO/ERBO increases the torque developed decreases correspondingly. The Brabender torque developed is reasonable (about 30 Nm) for mixes having 5 phr levels of DOP/RBO/ERBO (Figs.3.1, 3.2, 3.3). Hence 5 phr levels of each of these oils can be taken as the optimum level for the compounding of NBR. For CR mixes also the torque developed is reasonable (about 30 Nm) when 4 phr of aromatic oil/RBO/ERBO were used (Figs. 3.4, 3.5 and 3.6). Hence 4 phr each of these oils can be taken as the optimum level for the compounding of CR. In each case the torque generated is more or less similar when RBO/ERBO replaces DOP/aromatic oil indicating that RBO/ERBO can be used as a processing aid for nitrile and polychloroprene rubbers used in this study. The reduction of torque on the addition of accelerator for CR mixes unlike in NBR is due to the fact that sulphur is not included in CR mixes. During the preparation of the NBR and CR compounds in a two roll mill 5 and 4 phr levels each of these oils respectively are found to be sufficient for the proper mixing of the ingredients.

Cure characteristics

The cure characteristics of the NBR and CR mixes were determined at 160°C and 150°C respectively, using a Goettfert Elastograph Model 67.85. The cure curves of NBR mixes using DOP are given in Fig. 3.7 and those with RBO are given in Fig. 3.8. Their cure characteristics are given in Table 3.3. The cure curves obtained by using different levels of DOP and ERBO are given in Fig. 3.9. From the cure curves it is evident that no compound shows reversion, irrespective of the processing aids used. From the figures it is clear that the maximum torque developed is higher in the mixes containing DOP compared to ones containing RBO/ERBO. The lower torque values in mixes containing RBO/ERBO might be attributed to the presence of the long paraffinic chains of the acids present in the oil which has effect as an internal lubricant. The optimum cure time of these mixes prepared with RBO/ERBO are also appreciably less compared to those with DOP. This can be considered as an added advantage when RBO/ERBO is used as processing aid instead of DOP for nitrile rubber. For chloroprene rubber, cure curves with aromatic oil are given in Fig. 3.10 and those with RBO in Fig. 3.11. And their cure characteristics are given in Table 3.4. The cure curves for CR mixes having different levels of aromatic oil/ERBO are given in Fig. 3.12. From the figures it is evident that all the compounds of chloroprene rubber give a marching cure curve irrespective of the processing aid used. The torque developed is more or less similar for the mixes prepared with aromatic oil/RBO. But in the case of mixes prepared with ERBO, the torque developed is significantly lower compared to the ones prepared with aromatic oil. This may be due to the greater lubricating effect of ERBO over aromatic oil. However, the optimum cure time of mixes with RBO/ERBO are lower than that with aromatic oil. These results clearly indicate the cure accelerating effect of rice bran oil/epoxy rice bran oil in both NBR and CR vulcanization systems. The reduction in cure time and hence the increased cure rate index observed when DOP/aromatic oil was substituted by RBO may be explained to be due to the presence of various amounts of different kinds of fatty acids present in the oil which might have an influence in the vulcanisation reaction of NBR and CR. It is also noted that in all the mixes of NBR and CR; replacement of the conventional process oils with rice bran oil/epoxidised rice bran oil does not affect the scorch characteristics adversely. The minimum torque value, a measure of the stock viscosity is lower for all the mixes prepared with RBO/ERBO compared to the respective control mixes, clearly indicating the improved processability afforded by rice bran oil and epoxidised rice bran oil.

Table 3.3 Cure characteristics of NBR mixes

	Mix No							
	D_0	D_1	D_2	D_3	R_0	R_1	R_2	R_3
Maximum torque MH_F (Nm)	0.51	0.48	0.62	0.67	0.41	0.30	0.37	0.27
Minimum toqrue ML (Nm)	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.04
$MH_F - ML$ (Nm)	0.46	0.43	0.57	0.62	0.37	0.26	0.33	0.23
Optimum cure time t_{90} (min)	3.32	3.10	3.40	3.40	3.20	2.70	2.80	2.30
Elastographic scorch time t_{10} (min)	1.90	1.90	1.90	1.90	1.80	1.70	1.80	1.60
Cure rate index	70.40	83.30	67.00	67.00	71.00	100.00	100.00	143.00

Table 3.4 Cure characteristics of CR mixes

	Mix No							
	C_0	C_1	C_2	C_3	RC_0	RC_1	RC_2	RC_3
Maximum torque MH_F (Nm)	0.59	0.53	0.49	053	0.57	0.59	0.54	0.51
Minimum toqrue ML (Nm)	0.06	0.05	0.05	0.05	0.04	0.04	0.05	0.04
$MH_F - ML$ (Nm)	0.53	0.48	0.44	0.48	0.53	0.55	0.49	0.47
Optimum cure time t_{90} (min)	18.70	19.00	19.20	19.30	17.30	17.50	17.40	17.60
Elastographic scorch time t_{10} (min)	1.40	1.40	1.60	1.50	1.30	1.40	1.30	1.30
Cure rate index	5.78	5.68	5.68	5.61	6.25	6.09	6.21	6.13

Table 3.5 Cure characteristics of NBR mixes with different levels of DOP/ERBO

	DOP 3 phr	DOP 5 phr	DOP 7 phr	ERBO 3 phr	ERBO 5 phr	ERBO 7 phr
Maximum torque MH_F (Nm)	0.56	0.51	0.49	0.42	0.37	0.32
Minimum torque ML (Nm)	0.06	0.05	0.05	0.04	0.04	0.04
MH_F - ML (Nm)	0.50	0.46	0.44	0.38	0.33	0.28
Optimum cure time t_{90}(min)	3.9	3.3	3.2	2.7	2.4	2.2
Elastographic scorch time, t_{10}(min)	2.0	1.9	1.9	1.8	1.8	1.8
Cure rate index	52.6	71.4	76.9	111.1	166.6	250

Table 3.6 Cure characteristics of CR mixes with different levels of aromatic oil/ERBO

	Aromatic oil 2 phr	Aromatic Oil 4 phr	Aromatic oil 6 phr	ERBO 2 phr	ERBO 4 phr	ERBO 6 phr
Maximum torque MH_F (Nm)	0.62	0.59	0.56	0.52	0.48	0.40
Minimum torque ML (Nm)	0.07	0.06	0.06	0.05	0.05	0.05
MH_F-ML (Nm)	0.55	0.53	0.50	0.47	0.43	0.35
Optimum cure time t_{90} (min)	19.5	18.7	18.2	17.5	17.0	16.0
Elastographic scorch time t_{10} (min)	1.5	1.5	1.5	1.4	1.4	1.4
Cure rate index	5.56	5.81	5.99	6.21	6.41	6.85

Replacing stearic acid from the NBR mix containing DOP (D_2) causes reduction in cure rate compared to control mix Do, whereas, similar change in the mix containing RBO (R_2) causes decrease of cure time value and corresponding increase in cure rate compared with control mix (D_o). Replacing stearic acid in the polychloroprene rubber mix (C_2) containing aromatic oil results in increase in optimum cure time but similar changes in the mix containing RBO (RC_2) causes a decrease in the cure time value compared to the control mix (C_o). These results and results reported in the subsequent sections clearly indicate that rice bran oil itself can effectively function as a co-activator even in the absence of stearic acid in both NBR and CR systems suggesting that the higher fatty acids present in rice bran oil are effective in these vulcanisation reactions. From Tables 3.5 and 3.6 it is also evident that like RBO, the epoxidised rice bran oil also has got cure accelerating effect apart from being a process aid in both nitrile and polychloroprene rubbers.

Crosslink density

The total chemical crosslink density of the various vulcanisates prepared with DOP/aromatic oil/RBO/ERBO was evaluated. The results obtained are given in Tables 3.7, 3.8, 3.9 and 3.10. Systems containing carbon black and rice bran oil showed lower crosslink density values than their respective control mixes. Similar trend is also shown by compounds prepared with epoxidised rice bran oil. This lower crosslink density values are seen reflected in the slightly lower tensile values of vulcanisates prepared with RBO/ERBO. The lower crosslink density values of the mixes prepared with RBO/ERBO over the respective control mixes may be attributed to the less polar character of RBO/ERBO compared to the other oils.

Tensile and other physical properties

The tensile and other physical properties obtained for the vulcanisates from the NBR and CR systems are given in Table 3.7, 3.8, 3.9 and 3.10. From the tables it is seen that in both NBR and CR systems the initial tensile strength is slightly higher for the vulcanisates prepared with DOP/aromatic oil than the ones prepared with RBO/ERBO. This behaviour is seen reflected in their respective crosslink density values also. For NBR vulcanisates the elongation at break is higher for mixes with RBO (R_2, R_3) than the corresponding mixes with DOP (D_2, D_3), which might be due to the higher internal lubrication and hence more chain flexibility afforded by the rice bran oil. When DOP was replaced with ERBO for NBR the elongation at break values were found to be decreased. However, for CR rubber the replacement of aromatic oil with ERBO resulted in an increase in elongation at break values. Aging studies of the RBO based NBR mixes with antioxidant (R_o, R_2) and without antioxidant (R_1) showed better ageing resistance (high value of percentage retention) compared to corresponding mixes containing DOP. Similar trend is observed in the CR mixes too, which also indicate the antioxidant properties of the phenols present in the rice bran oil. Ageing studies on the vulcanisates prepared with different levels of ERBO for the NBR and CR systems showed that the percentage retention of tensile strength as well as elongation at break values (Tables 3.9 and 3.10) are higher for these systems than the corresponding ones prepared with DOP/aromatic oil. These results are indicative of the better heat stability of the ERBO over the other processing aids. This improved heat stability of ERBO may be attributed to the presence of oxirane rings in the oil and corresponding reduction in the unsaturation.

Table 3.7 Physical properties of NBR vulcanisates

	Mix No							
	D_0	D_1	D_2	D_3	R_0	R_1	R_2	R_3
Tensile strength (MPa) BA	23.16	23.89	26.45	26.76	22.61	24.41	25.66	25.81
Tensile strength(MPa) AA	16.38	15.48	17.51	16.46	17.76	16.48	17.25	17.81
Retention (%)	70.72	64.79	66.20	62.00	78.55	67.51	67.20	69.00
Elongation at break (%) BA	397	353	390	345	393	354	415	439
Elongation at break (%) AA	164	156	174	141	162	142	163	171
Modulus at 200% (MPa)	9.48	11.14	9.87	12.51	8.61	11.42	8.86	8.34
Tear strength (N/mm)	74.00	72.00	72.00	76.00	70.00	69.00	71.00	73.00
Compression set (%)	19.00	20.00	20.00	21.00	19.00	19.00	20.00	18.00
Hardness (Shore A)	65	66	67	65	64	65	65	66
Abrasion loss (cm^3 / hr)	3.33	3.31	3.30	3.32	2.86	2.84	2.88	2.84
Crosslink density (gms mole / gm) x 10^{-5}	5.98	6.08	6.20	6.29	5.48	5.82	5.92	5.99

BA – Before ageing
AA – After ageing

Table 3.8 Physical properties of CR vulcanisates

	Mix No							
	C_0	C_1	C_2	C_3	RC_0	RC_1	RC_2	RC_3
Tensile strength (MPa) BA	18.20	19.53	20.53	20.04	17.09	17.28	18.86	18.15
Tensile strength(MPa) AA	16.78	15.75	18.37	16.83	16.29	15.52	18.14	16.80
Retention (%)	92.20	80.80	89.47	83.90	95.30	89.80	96.18	92.50
Elongation at break (%) BA	257	266	261	266	225	227	261	254
Elongation at break (%) AA	223	207	215	200	221	195	218	188
Modulus at 200% (MPa)	5.03	5.00	5.04	4.96	5.05	5.38	5.10	5.17
Tear strength (N/mm)	71.00	69.00	73.00	64.00	64.00	62.00	63.00	61.00
Compression set (%)	14.00	14.00	14.00	14.00	15.00	15.00	15.00	15.00
Hardness (Shore A)	61	62	63	63	64	64	64	64
Abrasion loss (cm^3 / hr)	2.90	2.94	2.98	2.98	2.48	2.52	2.57	2.56
Crosslink density (gms mole / gm) x 10^{-4}	1.51	1.56	1.58	1.59	1.44	1.48	1.56	1.53

BA – Before ageing
AA – After ageing

Table 3.9 Physical properties of NBR mixes prepared with DOP/ERBO

	DOP 3 phr	DOP 5 phr	DOP 7 phr	ERBO 3 phr	ERBO 5 phr	ERBO 7 phr
Tensile strength, (MPa) BA	23.84	23.16	22.42	21.72	17.56	16.55
Tensile strength, (MPa) AA	16.70	16.38	15.52	19.02	17.31	16.56
Retention (%)	70.00	71.00	69.00	88.00	99.00	100.00
Elongation at break, (%) BA	362.00	392.00	402.00	318.00	346.00	365.00
Elongation at break, (%) AA	158.00	164.00	168.00	189.00	209.00	249.00
Retention (%)	44.00	42.00	42.00	59.00	60.00	68.00
200% Modulus (Mpa)	9.82	9.48	9.12	11.10	8.88	8.33
Tear strength (Nmm^{-1})	74.00	74.00	76.00	72.00	73.00	74.00
Compression set (%)	20.00	19.00	19.00	18.00	17.00	17.00
Hardness (Shore A)	66.00	65.00	63.00	65.00	64.00	62.00
Abrasion Loss (cm^3/hr)	3.42	3.33	3.18	3.12	3.08	2.96
Crosslink density (gmsmole/gm) x 10^{-5}	5.62	5.58	5.42	5.41	5.12	4.95

Table 3.10 Physical properties of CR mixes prepared with aromatic oil/ERBO

	Ar.oil 2 phr	Ar.oil 4 phr	Ar.oil 6 phr	ERBO 2 phr	ERBO 4 phr	ERBO 6 phr
Tensile strength, (MPa) BA	19.60	18.20	17.21	19.72	18.62	16.33
Tensile strength, (MPa) AA	17.40	16.87	15.43	19.22	17.24	17.75
Retention (%)	89.00	92.00	90.00	97.00	93.00	109.00
Elongation at break, (%) BA	236.00	257.00	276.00	261.00	317.00	314.00
Elongation at break, (%) AA	216.00	223.00	238.00	254.00	286.00	295.00
Retention (%)	92.00	87.00	86.00	97.00	90.00	94.00
200% Modulus (MPa)	5.88	5.03	4.92	13.70	9.20	8.67
Tear strength (Nmm^{-1})	69.00	71.00	73.00	66.00	68.00	70.00
Compression set (%)	14.00	14.00	14.00	15.00	14.00	14.00
Hardness (Shore A)	63.00	61.00	59.00	62.00	60.00	58.00
Abrasion Loss (cm^3/hr)	3.42	3.33	3.18	3.12	3.08	2.96
Crosslink density (gmsmole/gm) x 10^{-4}	1.62	1.50	1.38	1.48	1.42	1.38

BA- Before ageing
AA- After ageing

Other physical properties like compression set, hardness (shore A), tear strength and abrasion loss values of the different vulcanisates of both NBR and CR were also estimated. It can be seen from the tables that hardness, compression set and tear strength values of NBR mixes containing aromatic oil/RBO/ERBO are more or less similar. This is true in similar CR mixes also. However, the abrasion loss values of NBR and CR vulcanisates with RBO/ERBO are lower than the DOP/aromatic oil based vulcanisates indicating better abrasion resistance of the former mixes. But this effect is less pronounced in the mixes prepared with ERBO compared to RBO. The better abrasion resistance of RBO/ERBO based vulcanisates of NBR and CR may be attributed to lower stiffness of these vulcanisate and better interaction of the filler with rubber in presence of RBO/ERBO. Based on these results it is reasonable to conclude that RBO/ERBO can be used in place of other conventional process aids in both NBR and CR vulcanization systems with not much adverse effects on processing parameters, cure characteristics and vulcanisate physical properties. Also noted is the fact that the higher fatty acids present in RBO can act as a co-activator and the natural phenols in the oil has satisfactory antioxidant properties in these rubber mixes.

CONCLUSION

From the processability studies using Brabender plasticorder, it is clear that rice bran oil/epoxidised rice bran oil can be effectively used in the compounding of both nitrile and chloroprene rubbers in place of conventional processing aids. The optimum cure time values of both NBR and CR mixes prepared with RBO/ERBO are found to be lower than that of the mixes prepared with DOP/aromatic oil, indicating that these oils exhibits cure acceleration in both the vulcanization studies under review. Study of the physical properties of the vulcanisate (before and after ageing) points to the fact that rice bran oil can very well replace conventional processing aids, fatty acid and antioxidant in NBR and CR compounds. The use of epoxidised rice bran oil imparts better ageing properties to the vulcanisates of both NBR and CR compared to the ones prepared with DOP/aromatic oil. Rice bran oil which is a natural product is non-toxic while some of the conventional plasticisers are reported to have toxic effects. Besides this RBO is available cheaper compared to the conventional plasticisers like DOP or aromatic oil.

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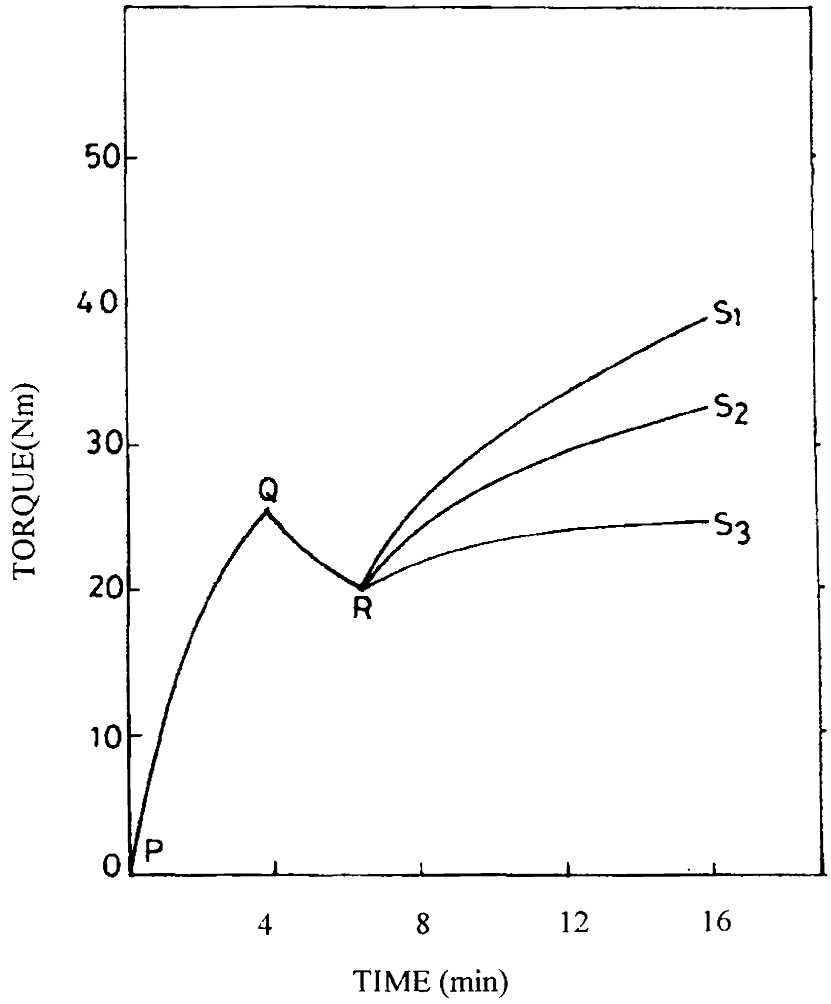

Fig. 3.1 Variation of Brabender torque with varying amounts of DOP in black filled NBR.
PQ - rubber; QR - sulphur and activator;
RS_1- carbon black, DOP (3 phr) and accelerator;
RS_2- carbon black, DOP (5 phr) and accelerator;
RS_3- carbon black, DOP (7 phr) and accelerator.

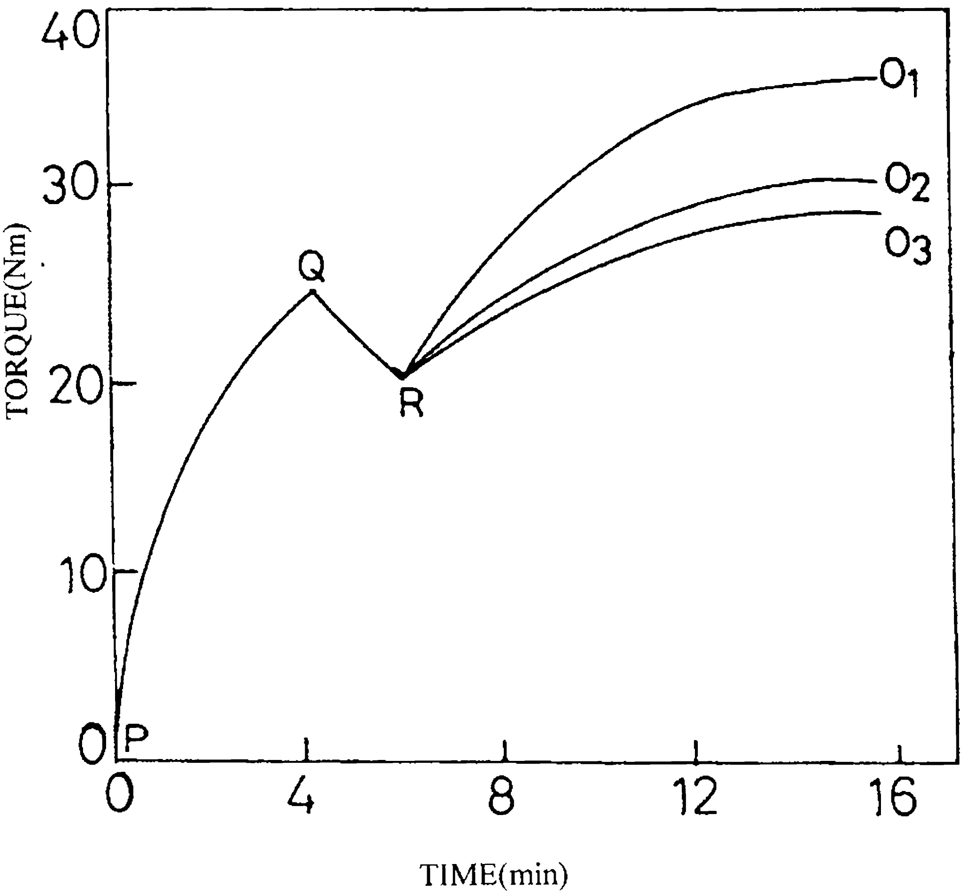

Fig. 3.2 Variation of Brabender torque with varying amounts of RBO in black filled NBR.
PQ - rubber; QR - sulphur and activator;
RO_1 - carbon black, RBO (3 phr) and accelerator;
RO_2 - carbon black, RBO (5 phr) and accelerator;
RO_3 - carbon black, RBO (7 phr) and accelerator.

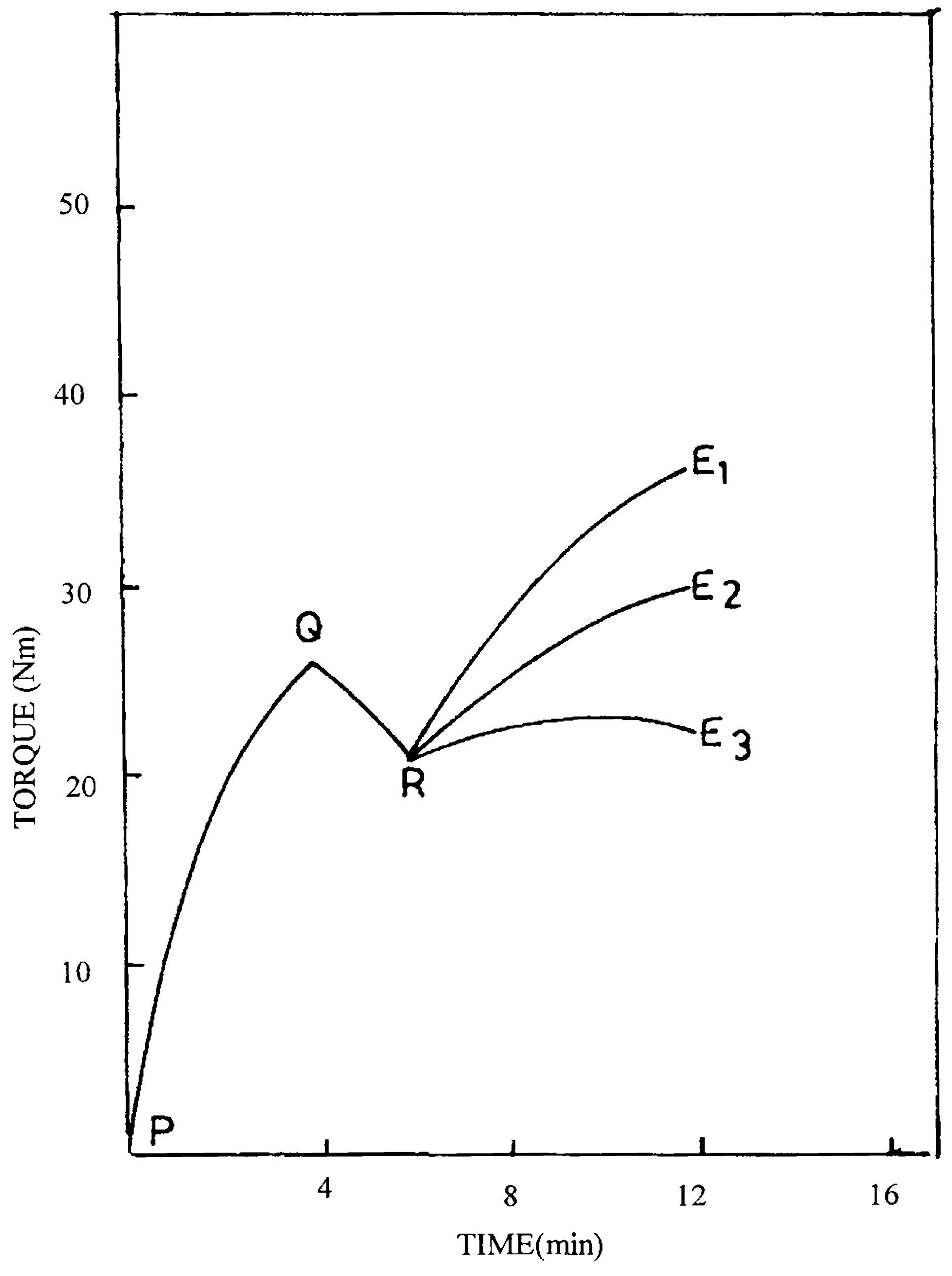

Fig. 3.3 Variation of Brabender torque with varying amounts of ERBO in black filled NBR.
PQ - rubber; QR - sulphur and activator;
RE_1- carbon black, ERBO (3 phr) and accelerator;
RE_2- carbon black, ERBO (5 phr) and accelerator;
RE_3- carbon black, ERBO (7 phr) and accelerator.

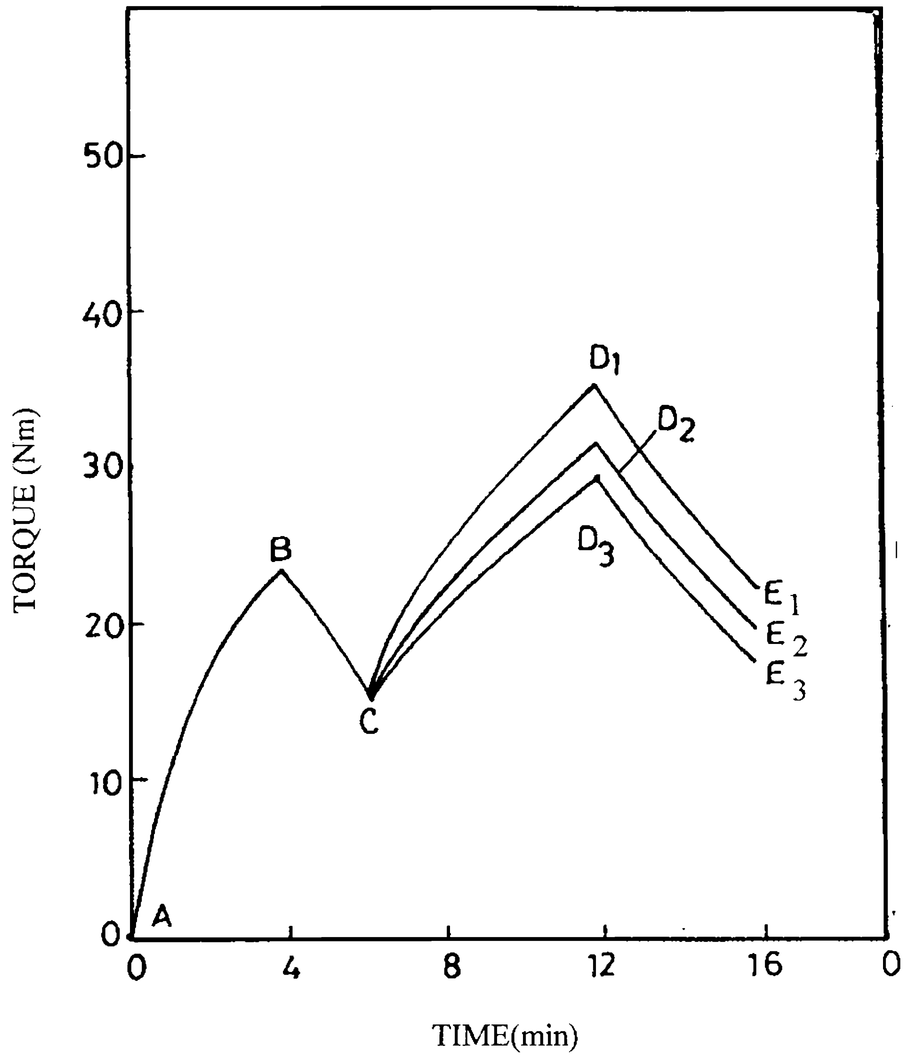

Fig.3.4 Variation of Brabender torque with varying amounts of aromatic oil in black filled CR.
AB - rubber; BC - MgO, ZnO and stearic acid;
CD_1 - carbon black, aromatic oil (2 phr);
CD_2 - carbon black, aromatic oil (4 phr);
CD_3 - carbon black, aromatic oil (6 phr).
D_1E_1, D_2E_2 and D_3E_3 - accelerator

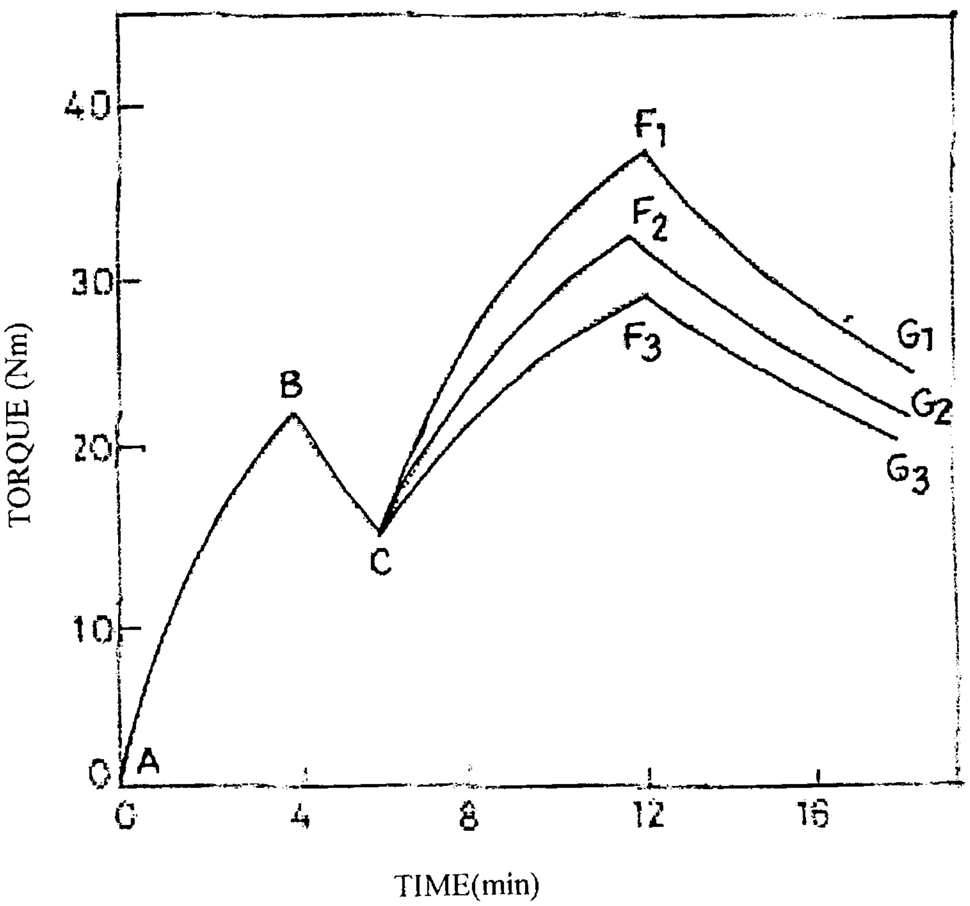

Fig.3.5 Variation of Brabender torque with varying amounts of RBO in black filled CR.
AB - rubber; BC - MgO, ZnO and stearic acid;
CF_1 - carbon black, RBO (2 phr);
CF_2 - carbon black, RBO (4 phr);
CF_3 - carbon black, RBO (6 phr). F_1G_1, F_2G_2 and F_3G_3 - accelerator

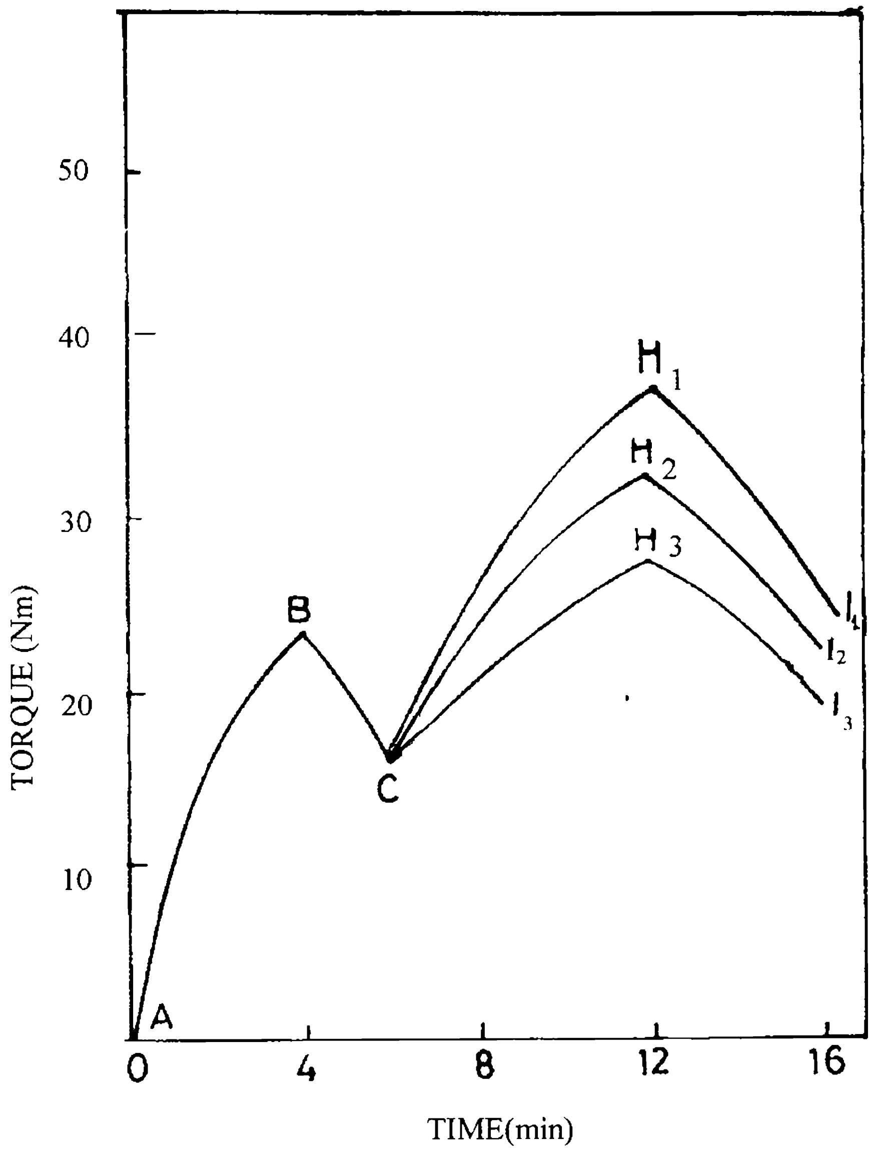

Fig. 3.6 Variation of Brabender torque with varying amounts of ERBO in black filled CR.
AB - rubber; BC - MgO, ZnO and stearic acid;
CH_1 - carbon black, ERBO (2 phr);
CH_2 - carbon black, ERBO (4 phr);
CH_3 - carbon black, ERBO (6 phr).
H_1I_1, H_2I_2 and H_3I_3 - accelerator

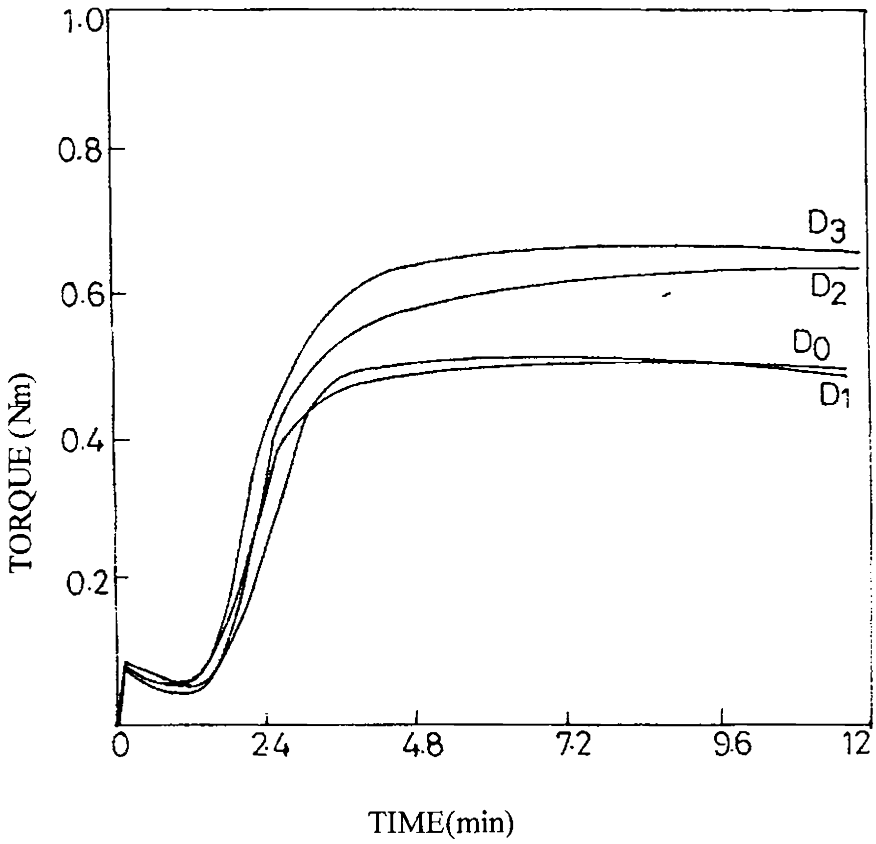

Fig. 3.7 Cure curves of NBR mixes containing DOP

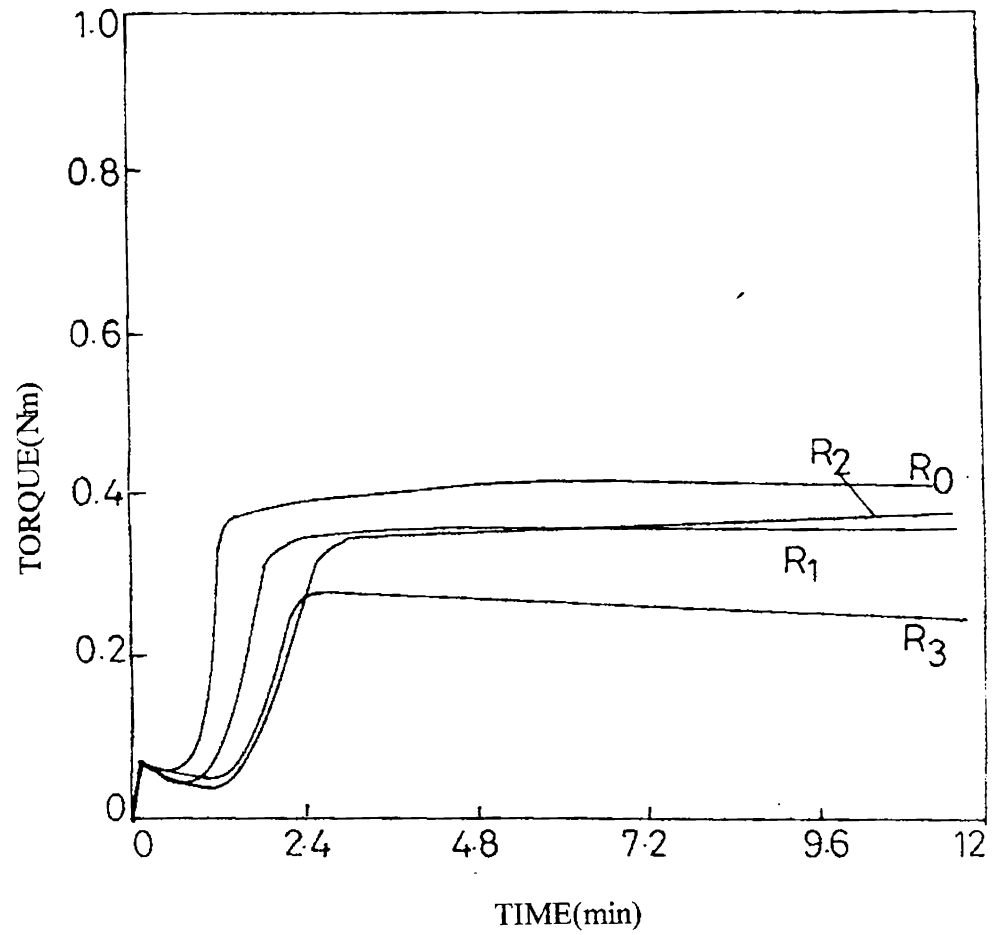

Fig. 3.8 Cure curves of NBR mixes containing RBO

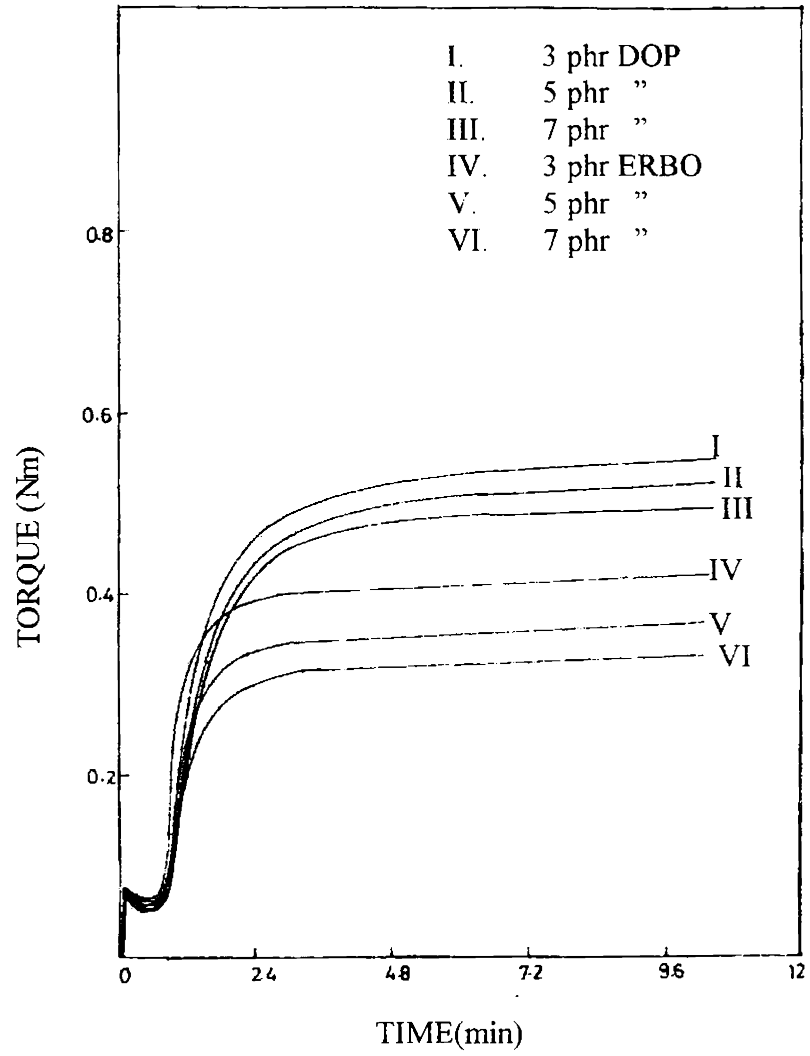

Fig. 3.9 Cure curves of NBR mixes with different levels of DOP/ ERBO

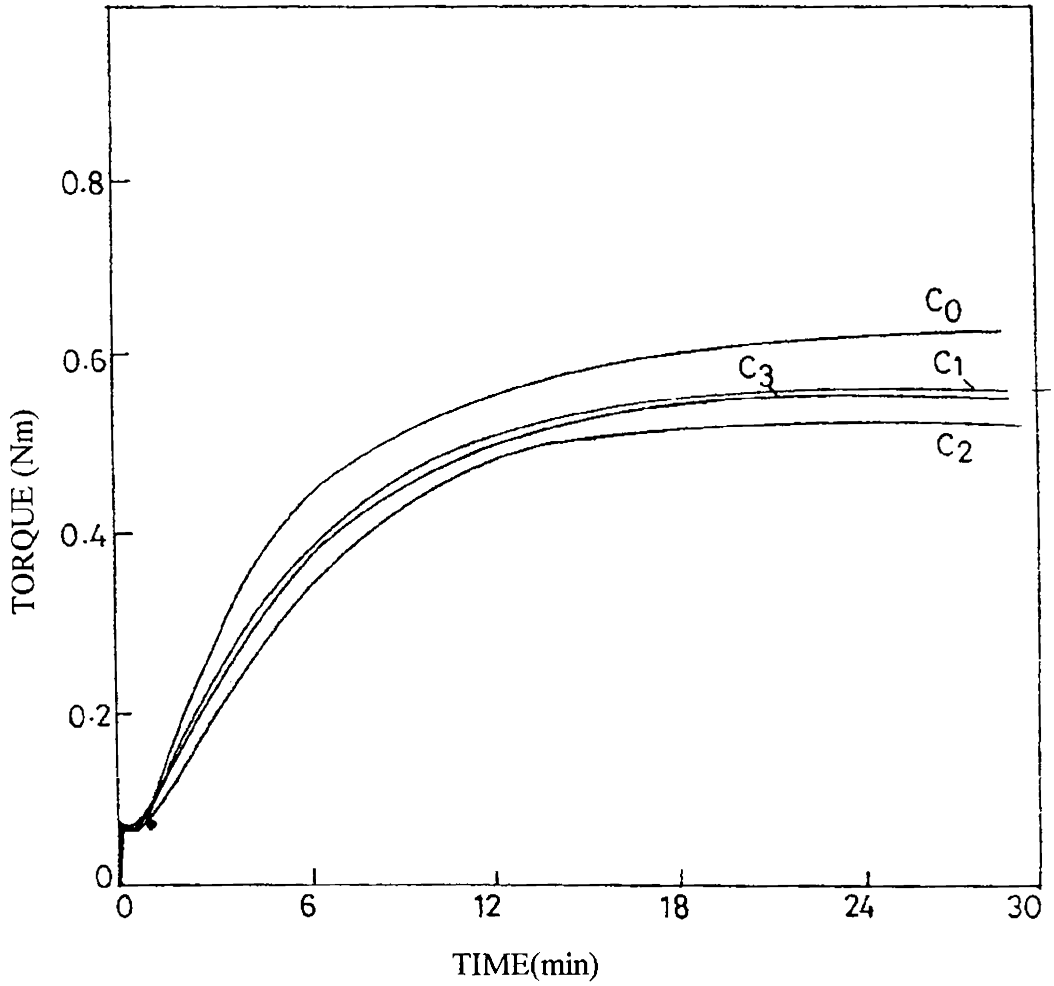

Fig. 3. 10 Cure curves of CR mixes containing aromatic oil

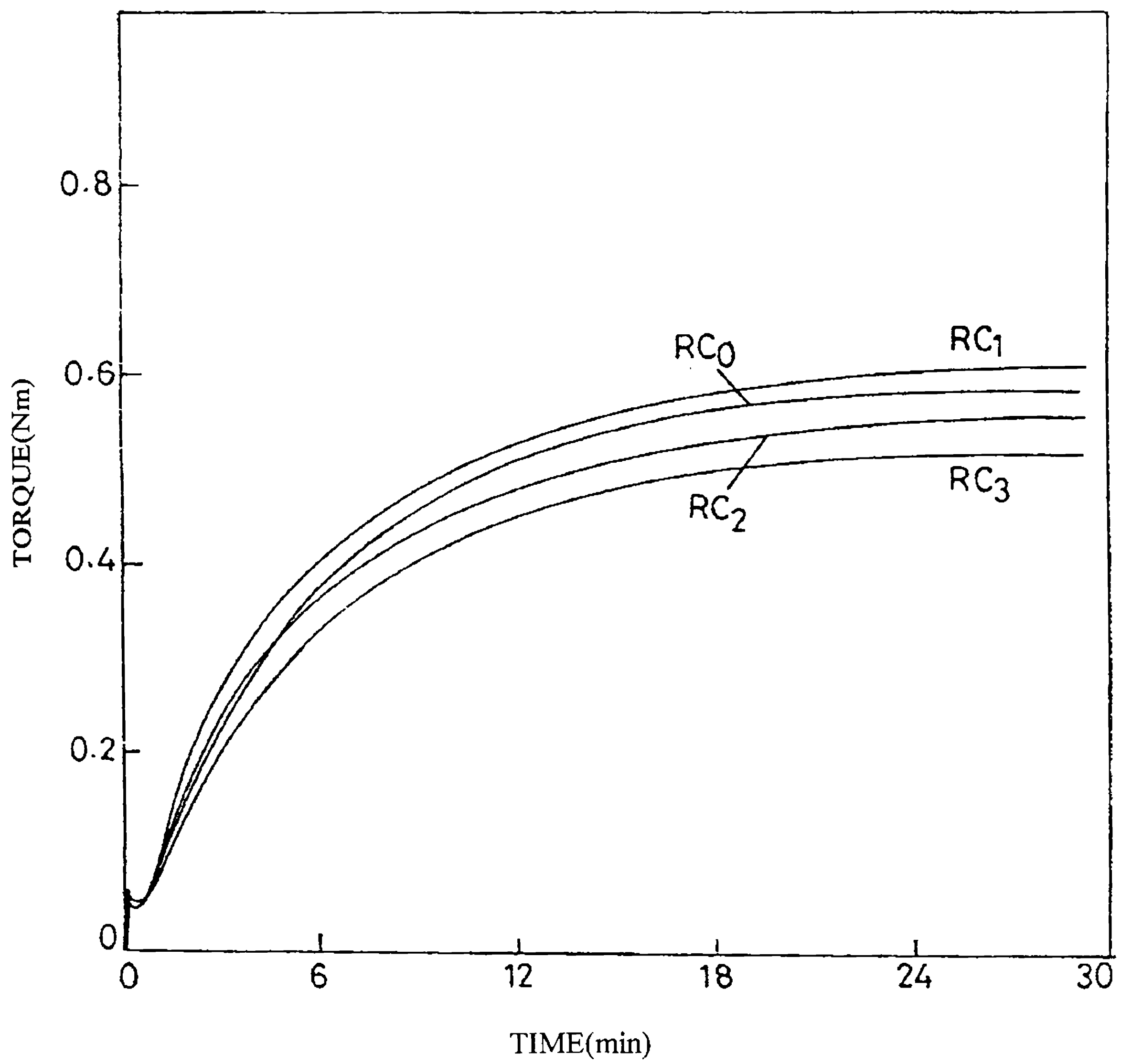

Fig. 3.11 Cure curves of CR mixes containing RBO

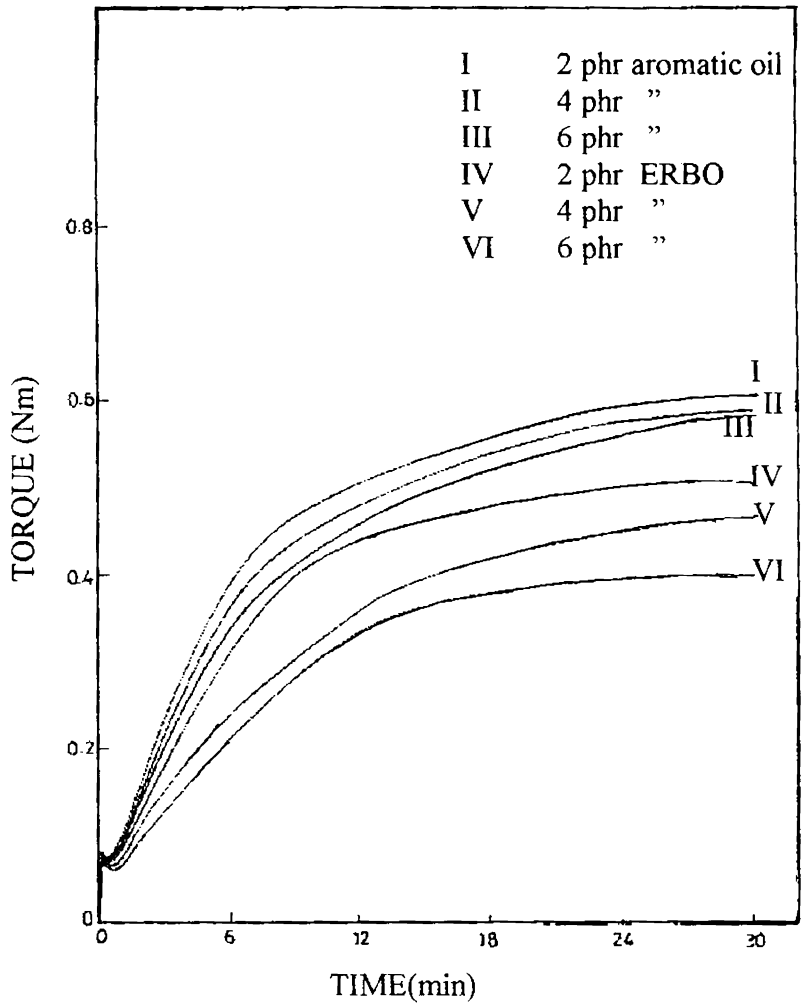

Figure 3.12 Cure curves of CR mixes with different levels of aromatic oil/ ERBO

CHAPTER IV

Chapter IV

STUDY ON THE USE OF RICE BRAN OIL/EPOXIDISED RICE BRAN OIL IN CARBON BLACK FILLED NR-CR BLENDS

Rubbers are blended for a variety of reasons viz: to obtain the right compromise in properties, to overcome the difficulty in processing and also for economic reasons. Blending of different elastomers is also an important technological process for improving the properties of the vulcanisates. Blends alone make up over 30% of the market for polymeric materials.[1] Blends of elastomers may be broadly classified into miscible and immiscible blends. Polymer scientists and engineers use the terms miscibility and compatibility rather loosely or interchangeably. In strict sense, thermodynamic miscibility describes polymer blends that are completely miscible and homogeneous down to the molecular level and which do not show any phase separation at all. By contrast, practical compatibility describes polymer blends which have properties that are useful in commercial practice. It should be emphasized that most of the commercially useful blends have practical compatibility, eventhough they do not have thermodynamic miscibility. Again it has been proved by phase contrast microscopic studies that many pairs of rubbers cannot be truly compatible on a molecular scale.[2] Theoretically, blends of chemically dissimilar (immiscible) elastomers can attain a wider variation in properties than blends of miscible and thus chemically similar elastomers.[3] Combination of immiscible elastomers lead to changes in properties, due to their intrinsic differences in the constituents or differences in the reinforcement and vulcanization of the constituents. Changing the properties of elastomers by uneven distribution of fillers and vulcanization is however, the more common use of blends of immiscible elastomers.[4] To obtain the optimum compromise in the properties of a rubber blend it is always better to use rubbers of closest solubility parameter values. However for purposes like damping applications rubbers with dissimilar solubility parameters give the desired low resilience compounds.[5] Such incompatible blends of dissimilar polymers like natural rubber (NR) and polychloroprene (CR) are found to have dynamic properties which are characteristic of the component of higher T_g at ambient temperature, but the lower T_g component appears to dominate at higher temperature.[6] In cases where NR is used for vibration isolation ie., under conditions where resonance may occur, a degree of damping is required. Blending of NR with a synthetic rubber of suitable T_g and cure characteristics is one of the techniques for increasing the damping characteristics of NR vulcanisates. An alternate method is to increase the loading of fine particle size fillers, and by addition of viscous aromatic oils. But the use of filler to increase hysteresis or damping is sometimes accompanied by undesirable increase in stiffness. To maintain modulus and hardness while increasing damping it is necessary to use a softener along with the filler and for this purpose a high viscosity grade aromatic process oil is advisable. Generally speaking the higher the aromaticity and viscosity of the oil the greater is the hysteresis.

The engineering properties of elastomers (tensile strength, hysteresis, shifts in loss tan peaks) in vulcanized compounds depend not only on the elastomer itself, but also on the amount and identity of the fillers and plasticisers, as well as on the extent of cure. In an immiscible blend, the amount of these additives in any phase can be modulated by changes in the viscosity and chemical identity of the elastomer, the surface chemistry of filler, the chemical nature of the plasticiser, the sequence of addition of the components and the details of the mixing procedure. Elastomers may be either preblended or phase mixed with each other.[7] Preblended systems are those in which the compounding ingredients (fillers, plastsicisers and curatives) are added simultaneously to a mixture of the immiscible polymers. In phase mixed blends ingredients are added separately to each of the individual polymers in separate compounding operations. The compounded elastomers are then blended together. Phase-mixed blends provide a greater certainty of the initial interphase location of fillers, plasticisers and curatives than do the preblends.

The detailed morphology of elastomer blends depends on the mixing procedure, the rheology of the components of the blend and the interfacial energy. The usual elastomer blend is a dispersion of one component in a matrix of the other. As with other polymer blends the elastomer of low viscosity tends to be the continuous phase.[8,9] Co-continuous blend morphology is observed only for elastomers with similar viscosities. During mixing curatives are initially located within the continuous phase.[10] Since the curatives dissolve in the elastomer, curative migration across phase boundaries can occur.[11] Owing to the higher solubility of sulphur in elastomers containing diene or styrene groups and the greater affinity of many accelerators for polar rubbers, large differences in crosslink density of the different phases result on vulcanization. At ambient and processing temperatures, elastomers are viscous fluids with persistent transport phenomena. In immiscible blends, these transport phenomena lead to changes in the size and shape of the elastomer phases and migration of the fillers, plasticizers, and curatives from one phase to another. These changes are accelerated by processing and plasticisation, but are retarded by the ultimate vulcanization.

The most common method of estimating the degree of homogeneity in elastomer blends is the measurement of the temperature of transition from rubber to glass (T_g). However, measurements of the T_g do not provide any information on blend morphology. The observation of distinct transitions, corresponding to the respective components of the blend, indicates the existence of multiple structure. A potential source of error is that vulcanization tends to raise the T_g of the blends, due to restricted motion of the chains and this increase in T_g might be interpreted as an indication of miscibility. The solubility parameters of normal process oils lie in the regions of 7.2 to 9.2. Here also polymer and oil combinations of similar solubility parameter are compatible. Oils may be used for reducing the Mooney viscosity, thus high Mooney rubbers can be oil extended for better mixing with low Mooney materials. Thus there is always the possibility of using oil to bridge the compatibility gap which exist between rubbers in a blend. Among other factors the requirements for rubber blends with vulcanisate properties arithmetically interpolated between those of the constituent rubbers are, rubbers having similar solubility parameter and similar viscosity. But choice of suitable plasticiser can offset slight deficiencies in the above mentioned factors.

In this part of the study the use of RBO/ERBO as a processing aid for improving the properties of black filled NR-CR blend is investigated. As reported earlier, RBO contains significant amount of free fatty acids, and an attempt has also been made in this study to see the effect of RBO as co-activator in addition to its role as processing aid in the compounding of this blend. The NR-CR blends prepared in different blend ratio using RBO/ERBO were evaluated for their cure characteristics and the vulcanisates were evaluated for tensile and other physical properties. The properties of the experimental mixes were compared with those of the control mixes prepared with aromatic oil. Heat ageing characteristics of the vulcanisates were also evaluated and compared with those of the control. Swelling index of the different vulcanisates was also estimated to evaluate the variation in the tensile properties of the different vulcanisates of the blends under review.

EXPERIMENTAL

Natural rubber and polychloroprene, having the specifications reported in chapter II is used in this study. Other compounding ingredients viz., ZnO, MgO, stearic acid, tetramethyl thiuram disulphide (TMTD), Ethylene thiourea (Na22), sulphur, carbon black (HAF 330), aromatic oil are all of rubber grade. Specifications of all the compounding ingredients used in the study are detailed in chapter II. The epoxidised rice bran oil prepared in our laboratory (having an oxirane content of 3.4%) is used for the compounding of the blend. In order to prepare ERBO, rice bran oil with a low FFA content and an iodine value of 92 was employed. The epoxidisation of the oil was effected with hydrogen peroxide in glacial acetic acid in presence of sulphuric acid as the catalyst. The experimental details are included in chapter II. For the determination of the epoxy content of the ERBO, a known weight of the ERBO is allowed to react with a known volume of excess hydrochloric acid and back titrating the residual HCl with standard alkali solution. By knowing the volume of HCl consumed the epoxy content was calculated.

The processing characteristics of the NR-CR blend with aromatic oil/rice bran oil/epoxidised rice bran oil was studied in a Brabender Plasticorder (PL3S) at 27°C. The initial speed of the roller mixing heads in the plasticorder was set at 40 rpm. The total weight of the blend including other compounding ingredients was restricted at 40 gms. NR and CR weighed according to their ratio in the blend was first passed six times in a two roll mill at a nip gap of 0.8 mm so as to get a thin sheet. This was then cut into small strips before feeding into the plasticorder. The total mixing time was kept at 16 min. with the following break-up. The rubber was first masticated for 4 min. followed by adding activator and accelerator within 3 min. Carbon black mixed with oil was then added within 8 min. and finally sulphur within 1 min. The formulation of the mix for each blend ratio under processability study (ie. 70/30; 50/50; 30/70 NR-CR) is as given in Table 4.1. Different levels (2,4,6 phr) of each of these oils was used for the blends under review. The final torque value is noted in all the cases. The experiment was repeated for 60 and 80 rpms also for all the blend ratios mentioned above. Flow curves are drawn by plotting viscosity (torque/rpm) against rotor speed.

After the processability study on the Brabender plasticorder the actual experimental mixes for vulcanization were prepared on a two roll mill (6"x12") as per ASTM D 3182-89 at friction ratio of 1:1.25 using the formulation given in Tables 4.1 and 4.2. For all the blend preparations an optimum of 4 phr of aromatic oil/RBO/ERBO was used as processing aid and was found to be sufficient for the proper mixing of the blend with the filler. For the preparation of the blend; NR was first masticated for 2 min. in the mill and then CR was added and again masticated for two minutes more so as to obtain a smooth band. MgO is then added followed by stearic acid and ZnO after a gap of one minute. This is then followed by antioxidant. Carbon black is then added within 5 minutes followed by processing aid and finally sulphur and accelerators are added within one minute. Mixes A_1 and R_1 are 50/50 NR-CR blend based on aromatic oil and RBO respectively without stearic acid. Mixes A_o and R_o are the corresponding mixes prepared with stearic acid. These four blends were selected to study the effect of RBO both in presence and absence of stearic acid in the blend properties especially the cure characteristics.

The swelling index, an indirect way of measuring total crosslink density, which in turn is correlated to the physical properties of the various vulcanisates was determined by immersing 0.2g of the sample in benzene for 24 hrs at room temperature and calculated using the equation as given below:

$$\text{Swelling index} = \frac{\text{Swollen weight - deswollen weight}}{\text{Original weight of sample}}$$

The cure characteristics of the various mixes at 150°C were evaluated using Goettfert elastograph (model 67.85). Details of the procedure is as given in chapter II.

Table 4.1 Formulation of the black filled NR-CR blend

Ingredients	NR-CR blend ratio				
	70/30	60/40	50/50	40/60	30/70
NR Phr	70	60	50	40	30
CR ”	30	40	50	60	70
ZnO ”	5	5	5	5	5
MgO ”	1.8	2.4	3.0	3.6	4.2
Stearic acid ”	1.55	1.40	1.25	1.10	0.95
Antioxidant ”	1.0	1.0	1.0	1.0	1.0
Sulphur ”	1.75	1.50	1.25	1.0	0.75
MOZ ”	1.12	0.96	0.80	0.64	0.48
TMTD ”	0.35	0.30	0.25	0.20	0.15
Na 22 ”	0.15	0.20	0.25	0.30	0.35
Aromatic oil/RBO/ERBO ”	4	4	4	4	4
Carbon black (HAF 330) ”	40	40	40	40	40

Table 4.2 Formulation of 50/50 NR-CR blend

Ingredients	Mix number			
	A0	A1	R0	R1
NR Phr	50	50	50	50
CR ”	50	50	50	50
ZnO ”	5	5	5	5
MgO ”	3	3	3	3
Stearic acid ”	1.25	0	1.25	0
Antioxidant ”	1.0	1.0	1.0	1.0
Sulphur ”	1.25	1.25	1.25	1.25
MOZ ”	0.80	0.80	0.80	0.80
TMTD ”	0.25	0.25	0.25	0.25
Na 22 ”	0.25	0.25	0.25	0.25
Aromatic oil ”	4	4	0	0
RBO ”	0	0	4	4
Carbon black (HAF 330) ”	40	40	40	40

The cure properties of the mixes are given in Table 4.3. Cure rate index, optimum cure time, scorch time, minimum torque, maximum torque etc. are reported therein. t_{90} is the optimum cure time (time to reach 90% of the maximum torque) and t_{10} is scorch time (time to reach 10% of the maximum torque). The cure rate index is calculated as

$$\frac{100}{t_{90} - t_{10}}$$

Vulcanisation was carried out in an electrically heated press of 18"x18" platens maintained at 150°C and at a pressure of 11.764 MPa. Tensile strength and elongation break were determined as per ASTM D 412-87 using a Zwick universal testing machine at a pulling rate of 500 mm/min. at 27°C. Dumbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Tear resistance was determined as per ASTM method D 624-86 using unnicked 90° test pieces. Ageing studies on the vulcanisates was carried out (ASTM D 573-88) at 100±1°C for 24 hrs in an air oven. Hardness was measured according to ASTM D 2240-86 and compression set according to ASTM D 395-86.

RESULTS AND DISCUSSION

Processability

In this part of the study, the variation in the processing characteristics brought about by using RBO/ERBO in place of aromatic oil in the compounding of black filled NR-CR blend in different blend ratio has been evaluated. The flow curves of the 70/30, 50/50 and 30/70 NR-CR blends based on the maximum torque (in Mgms) generated and 'rpm' used are given in Figs. 4.1, 4.2 and 4.3. In the figures the (torque/rpm) represents viscosity calculated on shear rate (rpm). The flow behaviour of the compound containing aromatic oil is more or less same as that of the compound containing RBO with similar pseudoplastic nature. However when 4 phr ERBO was used the torque developed is less compared to the mix where equal quantity of aromatic oil is used. Similar behaviour with respect to torque is noted with all the blend ratio under review. From the results it is evident that the maximum torque generated at 40 rpm is below 30 Nm, which is a reasonable value when 2, 4, 6 phr levels of RBO/ERBO/aromatic oil were used as processing aids irrespective of blend ratio. But during the actual compounding of the blend in a two roll mill it was found that a minimum of 4 phr each of these oils was necessary so that the heat generated during compounding can be controlled. In addition to this, at this level of processing aids, it was found that the filler intake to the polymer matrix also took place within reasonable time. Hence 4 phr of each of these oils can be taken as the optimum level. Estimation of cure characteristics of the mixes and physical properties of the vulcanisates reported later in this chapter also indicate that rice bran oil and epoxidised rice bran oil do not have any adverse effect on the vulcanization of the mixes.

Cure characteristics

Figures 4.4, 4.5 and 4.6 show the cure curves and Table 4.3 the different cure characteristics of the mixes prepared using aromatic oil/RBO/ERBO. From the figures it may be noted that the maximum torque developed is more or less same when aromatic oil/RBO were used as processing aid. The minimum torque values which is a measure of compound viscosity is also having more or less same values for the blends

4.3 Cure characteristics of NR-CR blends prepared with aromatic oil/RBO/ERBO

NR-CR blend ratio	Maximum torque (Nm)			Minimum torque (Nm)			Optimum cure time t_{90} (min)			Scorch time t_{10} (min)			Cure rate index		
	Mix with Aromatic oil	Mix with RBO	Mix with ERBO	Mix with Aromatic oil	Mix with RBO	Mix with ERBO	Mix with Aromatic oil	Mix with RBO	Mix with ERBO	Mix with Aromatic oil	Mix with RBO	Mix with ERBO	Mix with Aromatic oil	Mix with RBO	Mix with ERBO
70/30	0.54	0.56	0.45	0.05	0.04	0.04	2.90	2.50	2.70	1.40	1.30	1.30	67	83	71
60/40	0.50	0.41	0.37	0.05	0.04	0.03	3.40	3.20	3.10	1.60	1.50	1.40	56	59	59
50/50	0.29	0.35	0.24	0.04	0.05	0.02	5.60	5.20	5.30	1.60	1.50	1.40	25	27	26
40/60	0.32	0.32	0.30	0.04	0.04	0.04	9.00	8.30	8.80	1.50	1.40	1.40	13	15	14
30/70	0.39	0.36	0.33	0.05	0.04	0.04	17.00	15.80	16.00	1.60	1.50	1.40	6.5	7	7

Table 4.4 Cure characteristics of 50/50 NR-CR blends with and without stearic acid

Mix number	Maximum Torque (Nm)	Minimum Torque (Nm)	Optimum cure time t_{90} (min)	Scorch time t_{10} (min)	Cure rate index
A_0	0.29	0.04	5.6	1.6	25
A_1	0.35	0.05	6.4	2.2	23
R_0	0.35	0.05	5.2	1.5	27
R_1	0.39	0.05	5.9	2.0	26

Table 4.5 Physical properties of NR-CR blends with and without stearic acid

Mix number	Tensile Strength (MPa)		Elongation at break (%)	Modulus at 200% (MPa)	Tear Strength (N/mm)	Compression set (%)	Abrasion loss (cm^3/hr)
	BA	AA					
A_0	19.6	10.2	418	7.4	55	31	4.39
A_1	20.8	17.5	374	10.0	62	33	4.44
R_0	20.8	9.7	379	9.3	59	28	3.94
R_1	21.5	18.2	377	10.1	63	29	3.96

BA- Before aging
AA- After aging

prepared with these oils. However when ERBO was used as processing aid the torque values obtained are slightly less compared to the control mixes prepared with aromatic oil. These observations point to the better plasticising effect of ERBO over that of aromatic oil and RBO. From the cure curves of the blends at different blend ratio, it is also evident that none of the blends show any reversion characteristics irrespective of the processing aids used. The cure rate values for the blends prepared with RBO are better compared to those with aromatic oil. This result points to the cure accelerating effect of RBO, in addition to its role as processing aid for the preparation of the blend. The cure accelerating property of RBO can be attributed to the presence of different free fatty acids in the oil, which has a positive influence in the curing reactions. The scorch time values are slightly lower for the blends prepared with RBO/ERBO compared with the control mixes prepared with aromatic oil.

Tensile and other physical properties

Figure 4.7 shows a graphical representation of the variation of tensile strength values of the vulcanisates from the different blends using aromatic oil/RBO/ERBO. The tensile strength values increase when weight of NR in the blend increases. Blends prepared with aromatic oil/RBO/ERBO show more or less same tensile strength values. After ageing the vulcanisates at 100±1°C for 24 hrs the percentage retention of tensile properties is also found to be better for the vulcanisate prepared with ERBO (Fig.4.10). This may be attributed to the ageing resistance offered by ERBO by virtue of the presence of epoxy groups in the oil. The elongation at break values is more for the blends prepared with ERBO over the ones prepared with aromatic oil (Fig.4.8).

Modulus values are more or less same for the blends prepared with RBO and aromatic oil. Slightly lower modulus values are observed for the mixes containing ERBO (Fig.4.9). The percentage retention of elongation at break is also found to be better for the blends prepared with ERBO over the respective control mixes (Fig.4.11).

Compression set, tear strength and abrasion resistance of the vulcanisates were also evaluated as per relevant ASTM procedures. The results on these tests indicate that the value of tear strength and compression set are more or less same for the mixes containing rice bran oil/aromatic oil (Figs.4.12, 4.13). Tear values of the vulcanisates prepared with ERBO are found to be higher compared to the ones prepared with aromatic oil. The abrasion loss values of the vulcanisate prepared with RBO/ERBO were also found to be appreciably less (ie. higher abrasion resistance) compared to the control formulations (Fig. 4.14). This may be attributed to the better filler-rubber interaction in presence of RBO/ERBO. The swelling index values of the blends prepared with aromatic oil/RBO/ERBO are represented in Fig.4.15. From the results it is evident that vulcanisate prepared with ERBO show lower swelling index value and hence higher crosslink density (swelling index is inversely proportional to the crosslink density). This is seen reflected in the corresponding tensile and tear strength values also.

It is a well established fact that for the vulcanization of the rubber compounds to be effective, in addition to sulphur, other compounding ingredients like activator, co-activator, accelerators etc. are to be included in the recipe. In the conventional rubber vulcanization system ZnO plays the role of activator and stearic acid functions as co-activator. ZnO together with co-activator speeds up the vulcanization reaction. In order to assess the role of RBO as a co-activator (as the oil contains different higher fatty acids), 50/50 NR-CR blends were prepared with and without stearic acid (mixes R_o and R_1). The corresponding control mixes (A_o and A_1) were prepared using aromatic oil as per the formulation given in Table 4.2. The cure characteristics (Table 4.4) and physical properties (Table 4.5) of these mixes were compared. From Table 4.4 it is clear that the cure characteristics like optimum cure time, torque values etc. are not adversely affected when stearic acid was replaced from the blend formulation. But this is less pronounced in RBO based blends (R_o and R_1) compared to the control blends (A_o and A_1). From Table 4.5 it is clear that almost all the physical properties studied give more or less similar values both in presence and absence of stearic acid irrespective of the processing aids used. These results suggest that the higher fatty acids present in RBO can replace stearic acid for the preparation of the blends without compromising on the cure characteristics or physical properties of the vulcanisates.

CONCLUSION

Studies on the use of rice bran oil and epoxidised rice bran oil in the compounding of NR-CR blends at different blend ratios with carbon black showed that these oils could be advantageously used as a processing aids in place of aromatic oil. The cure characteristics of the blends prepared with RBO/ERBO showed that optimum cure time values are lower compared with the ones prepared with aromatic oil. The scorch time values are slightly lower when aromatic oil is replaced with RBO/ERBO. The torque values and compound viscosity is also appreciably less when ERBO was used in place of aromatic oil for the preparation of these blends. The cure characteristics and mechanical properties of the blends based on RBO suggest that this oil could be used even in the absence of stearic acid for the preparation of the blends without compromising in any of these properties. It may also be noted that non-edible RBO is appreciably cheaper compared to aromatic oil. In addition, RBO being a natural product is nontoxic, and environment friendly compared to mineral oils conventionally used for these applications. Moreover mineral oil resources are fast depleting and their cost also increases prohibitively.

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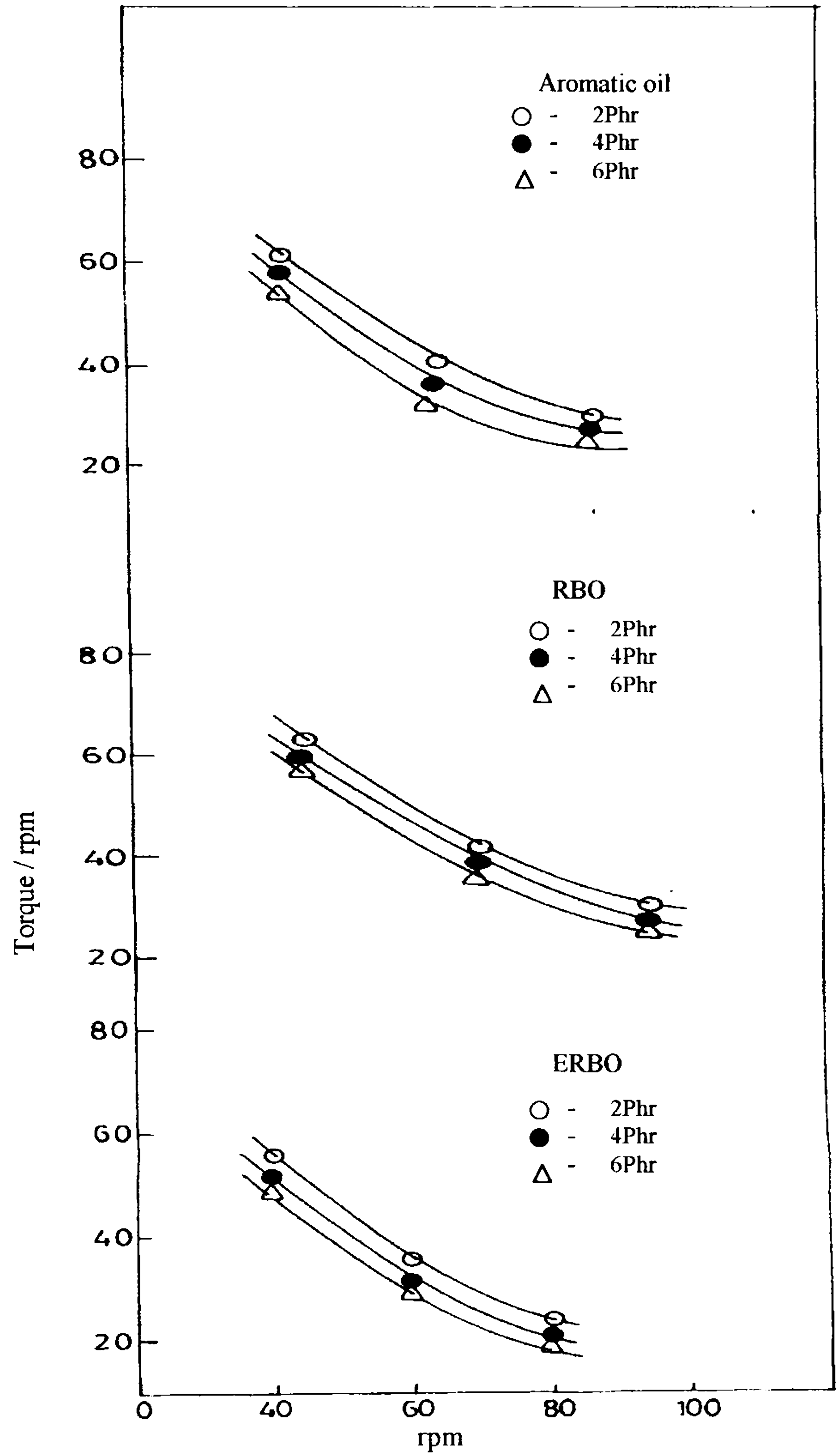

Fig. 4.1 Flow curves of black filled 70/30 NR-CR blends with different levels of aromatic oil/RBO/ERBO

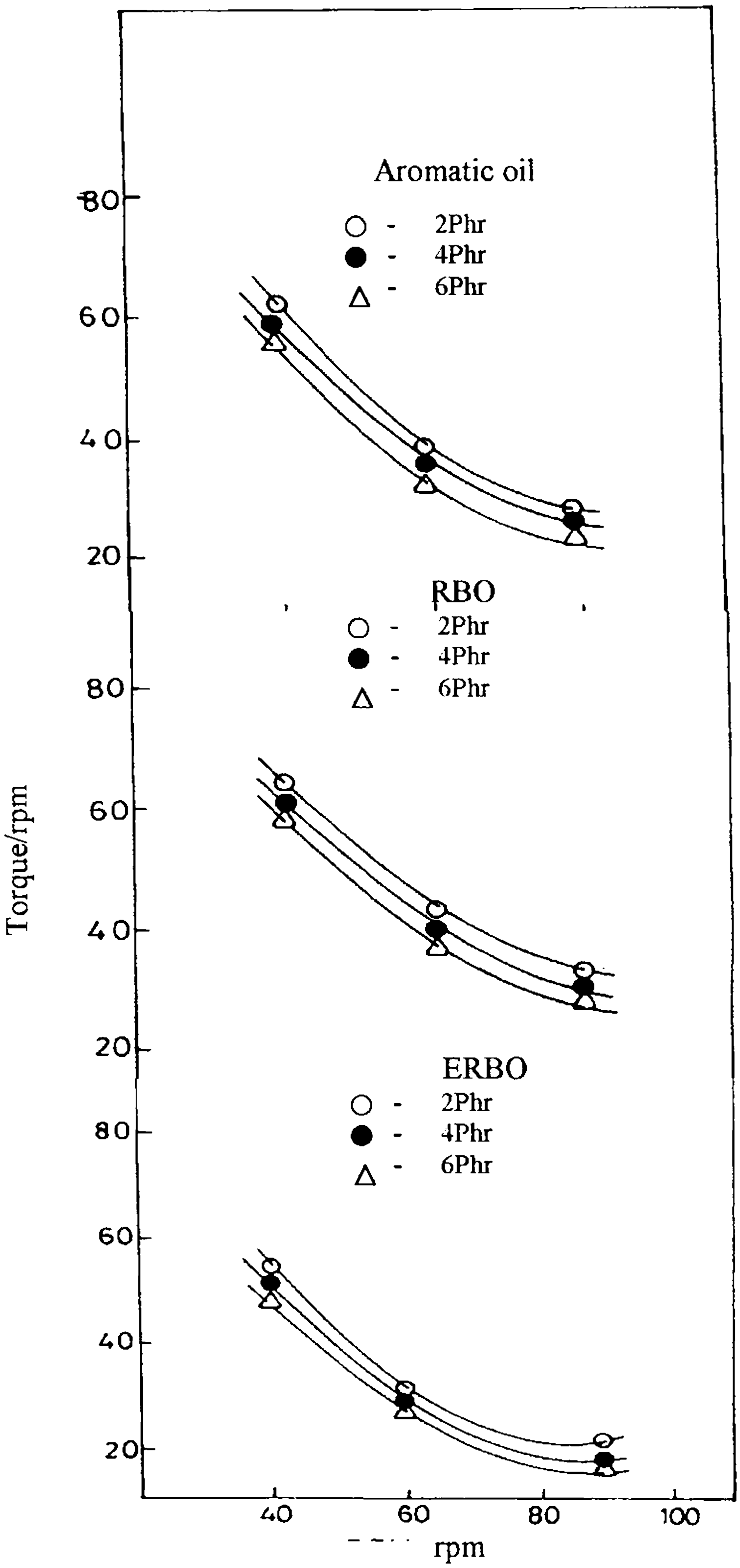

Fig. 4.2 Flow curves of black filled 50/50 NR-CR blends with different levels of aromatic oil/RBO/ERBO

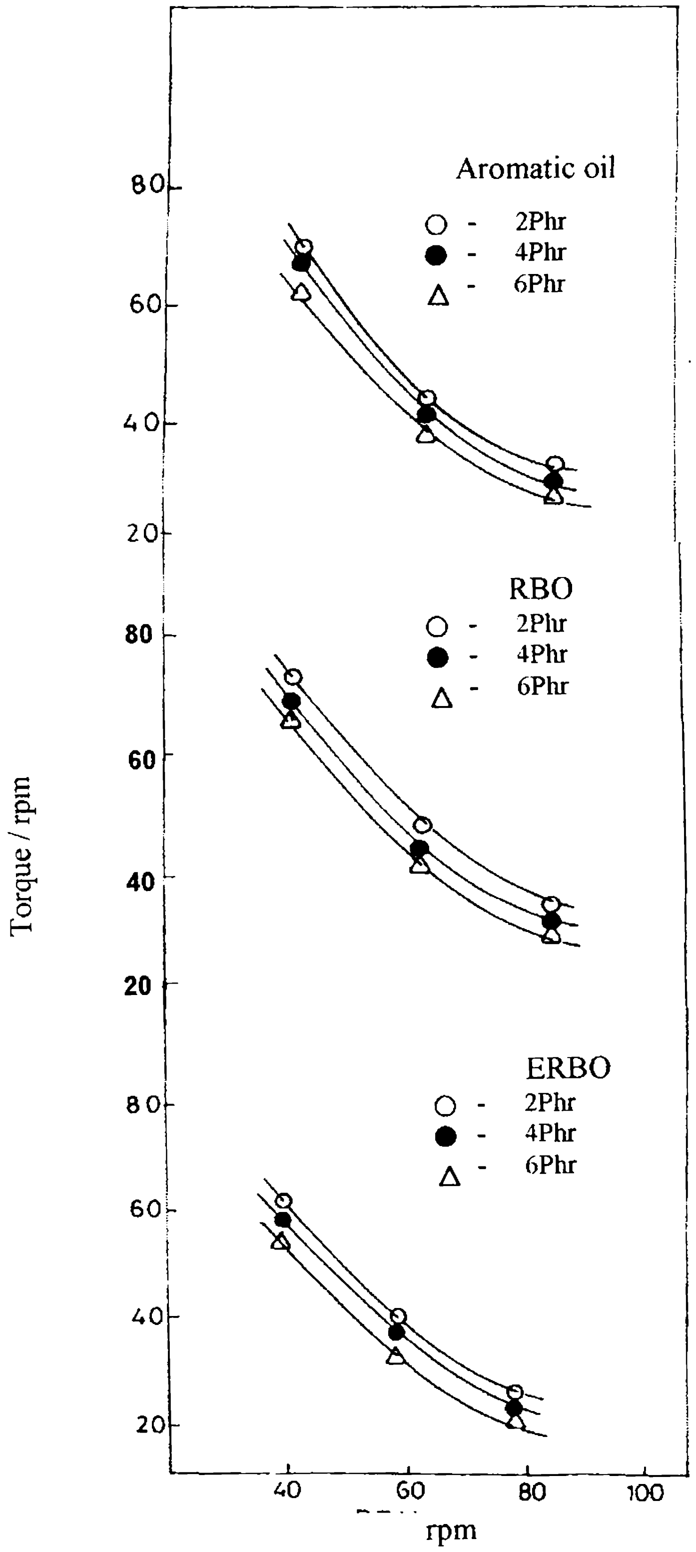

Fig. 4.3 Flow curves of black filled 30/70 NR-CR blends with different levels of aromatic oil/RBO/ERBO

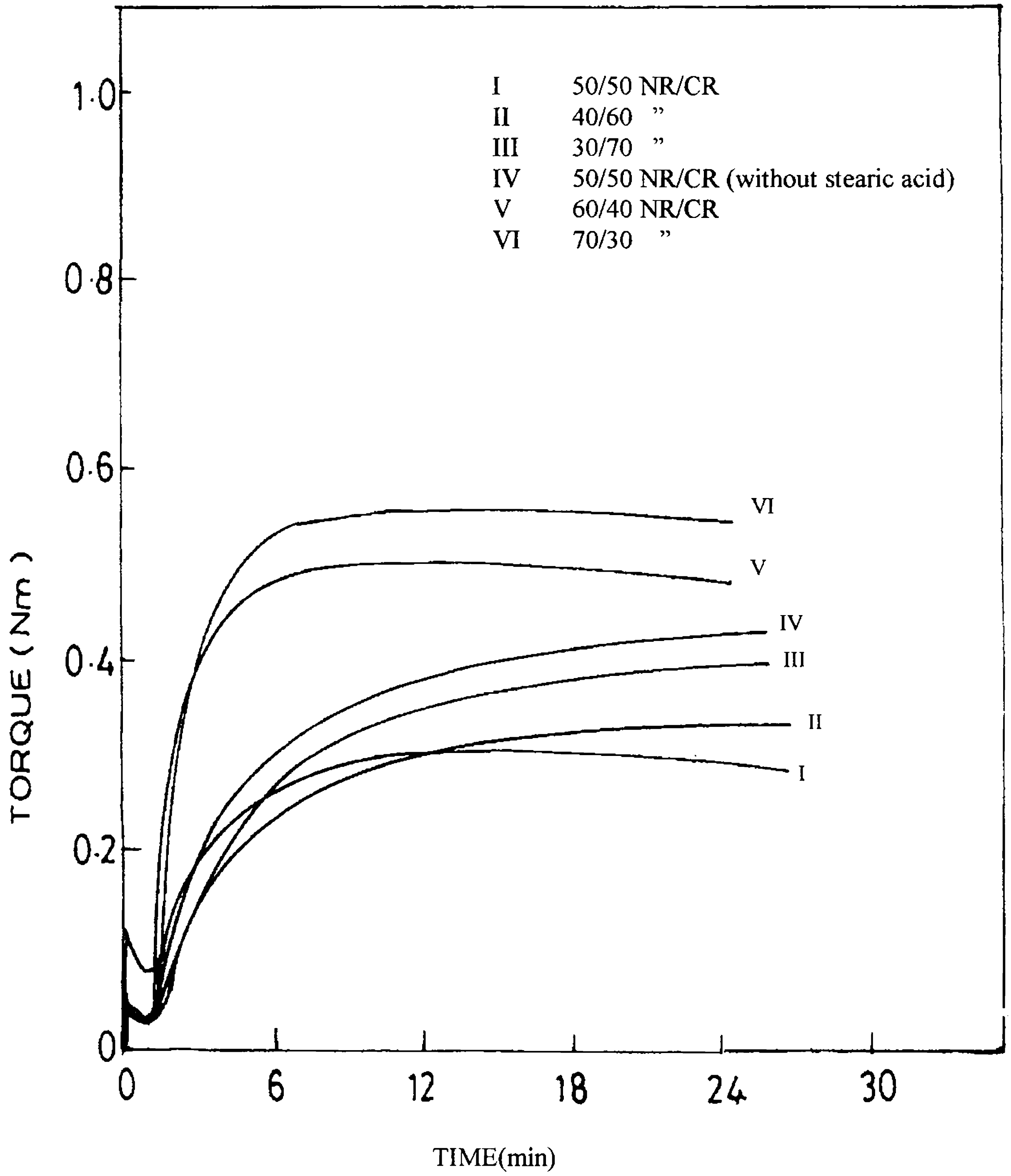

Fig. 4.4 Cure curves of NR-CR blends prepared with aromatic oil

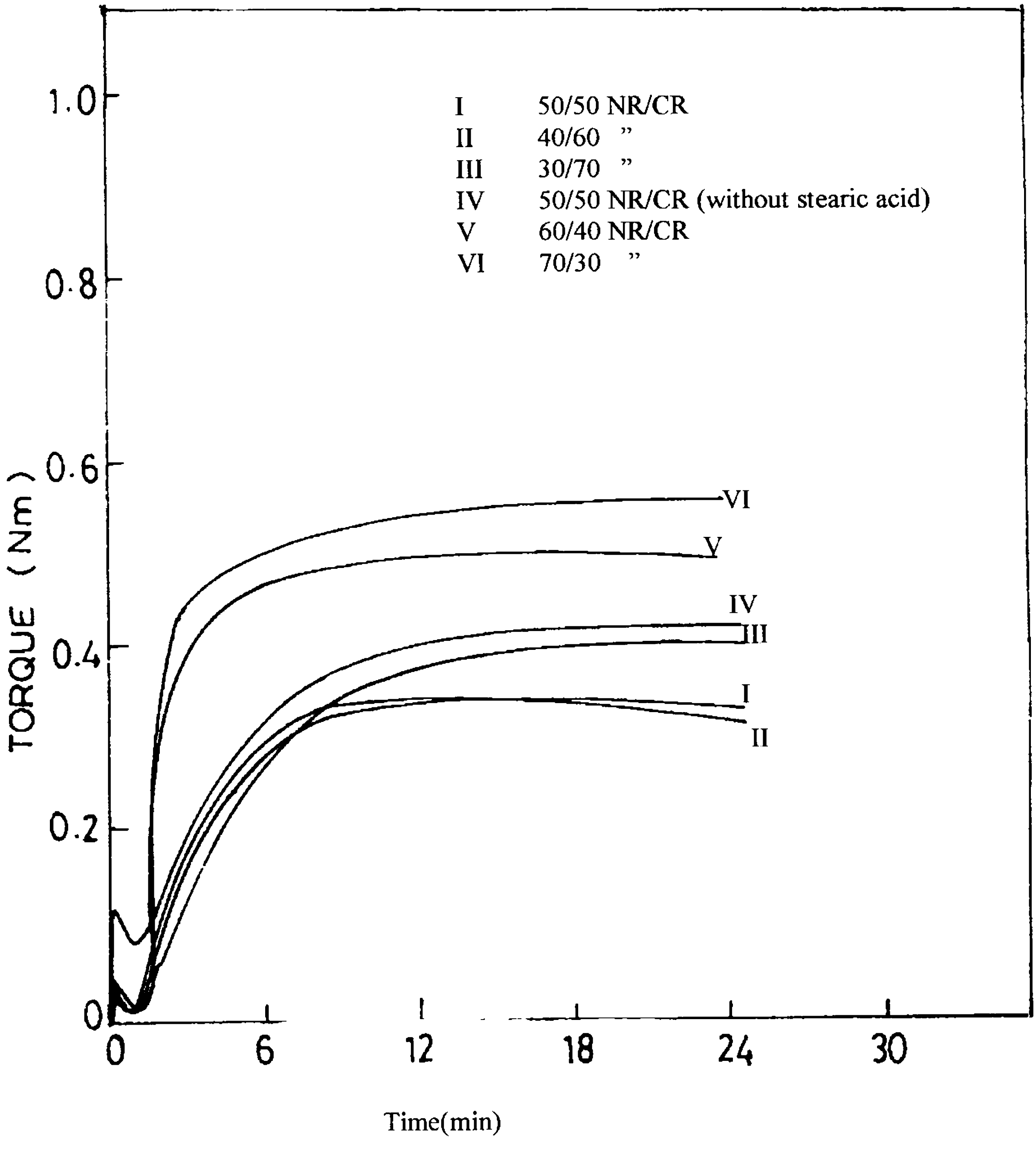

Fig. 4.5 Cure curves of NR-CR blends prepared with RBO

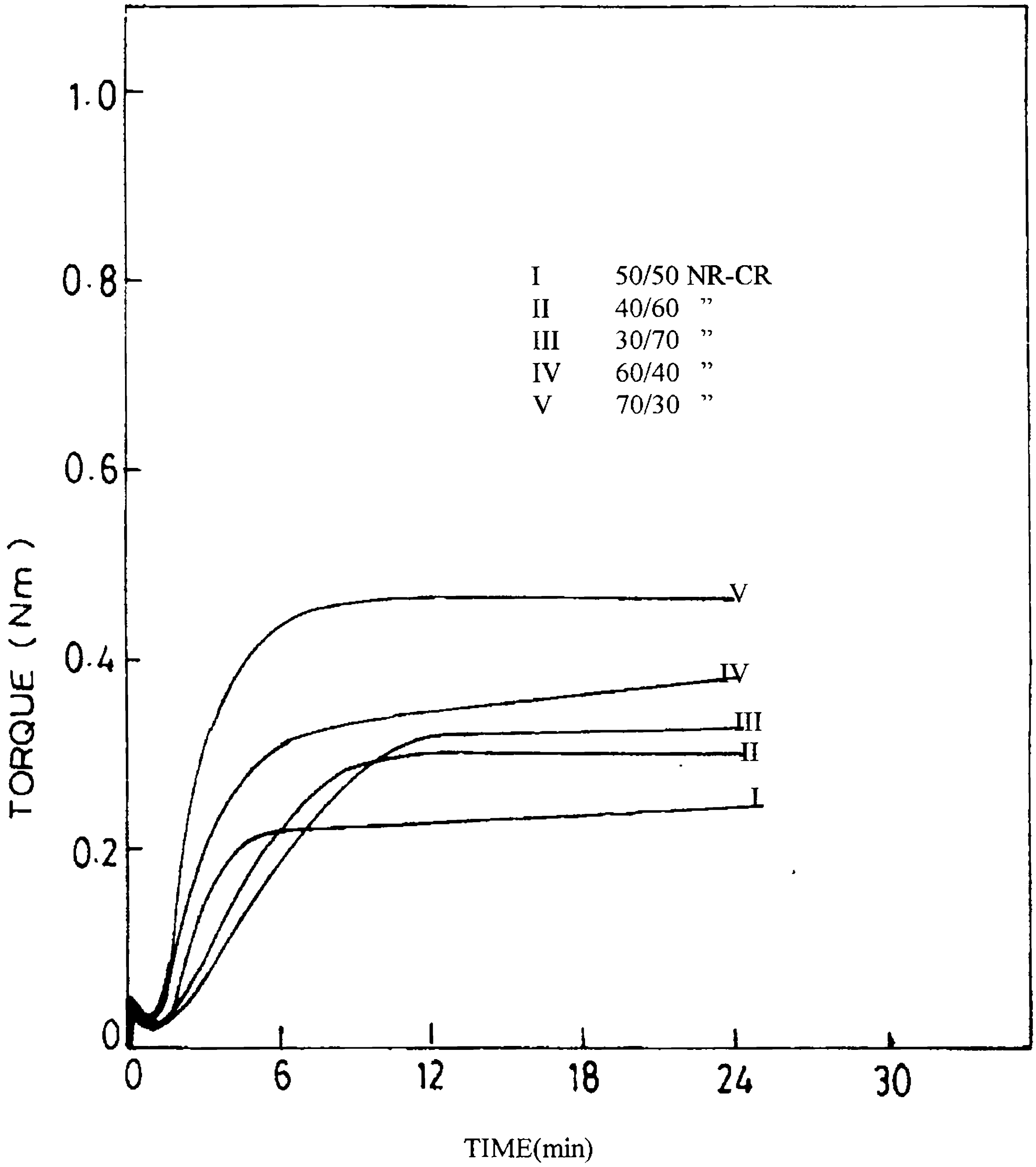

Fig.4.6 Cure curves of NR-CR blends prepared with ERBO

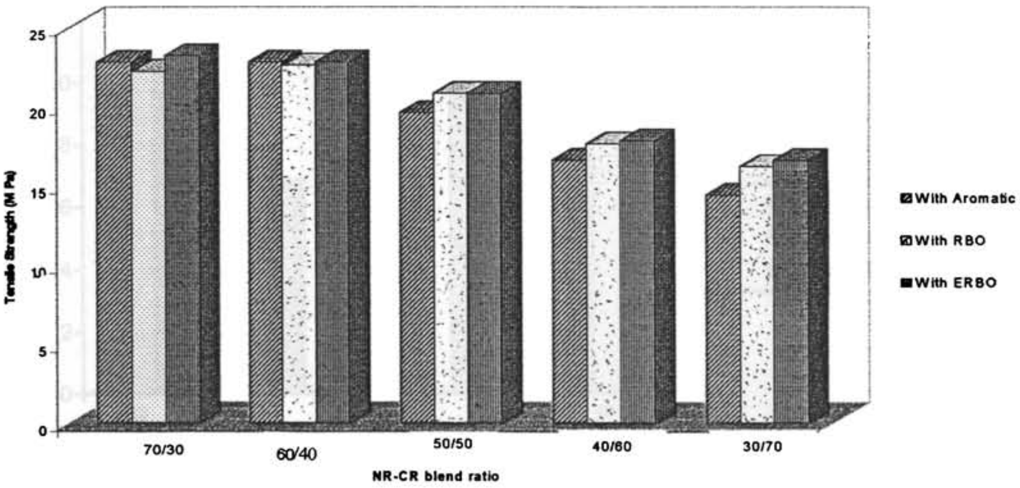

Fig. 4. 7 Variation of tensile strength values with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

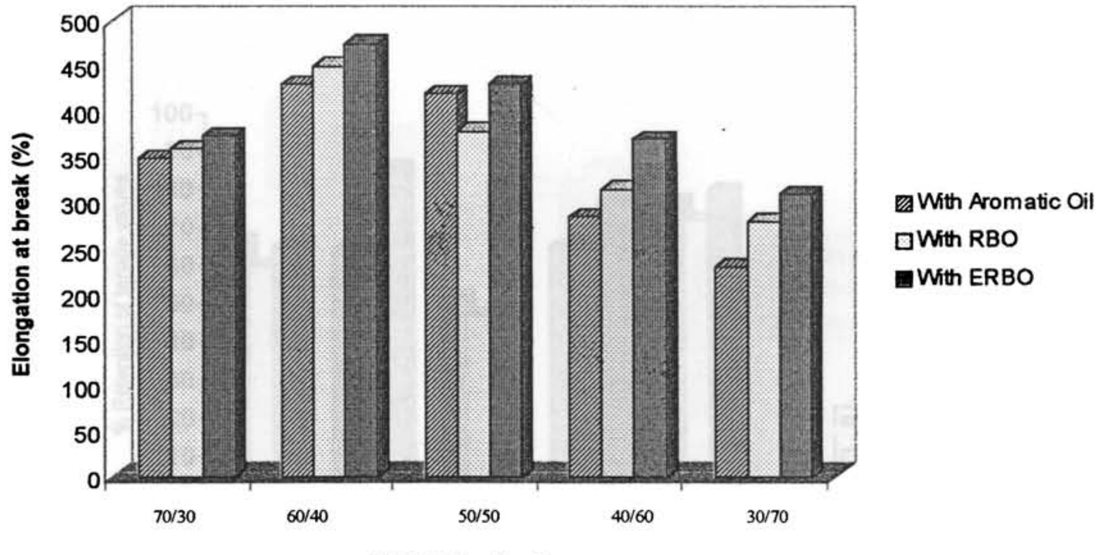

Fig. 4.8 Variation of EB values with blend ratio of NR-CR blends prepared with aromatic oil / RBO / ERBO

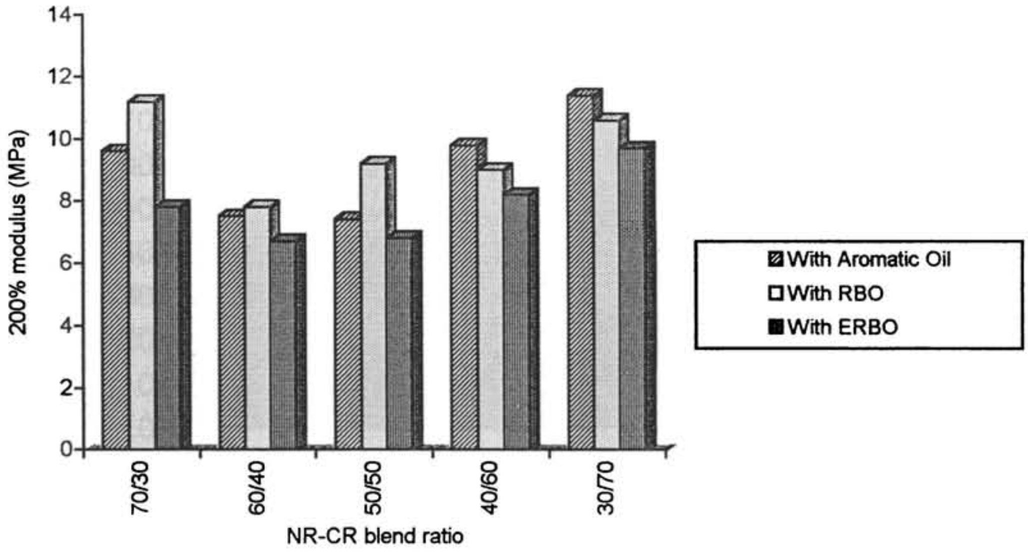

Fig. 4.9 Variation of 200% modulus with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

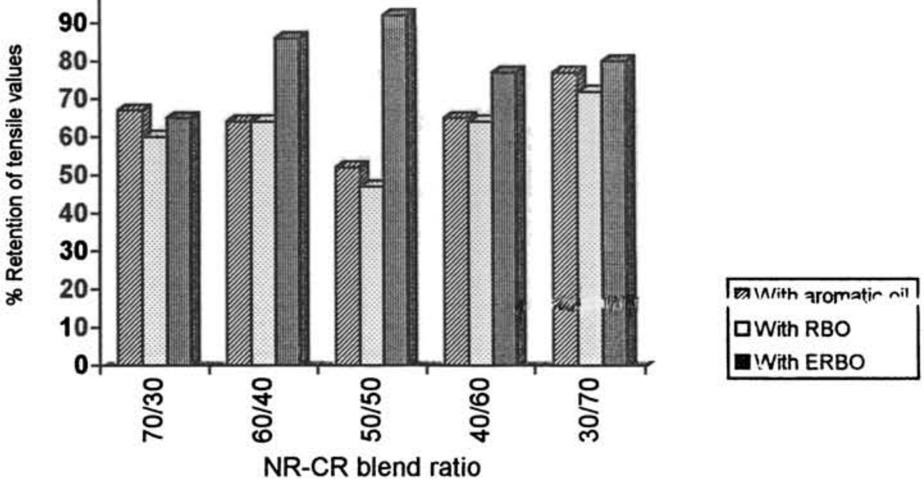

Fig. 4.10 Percentage retention of tensile strength values with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

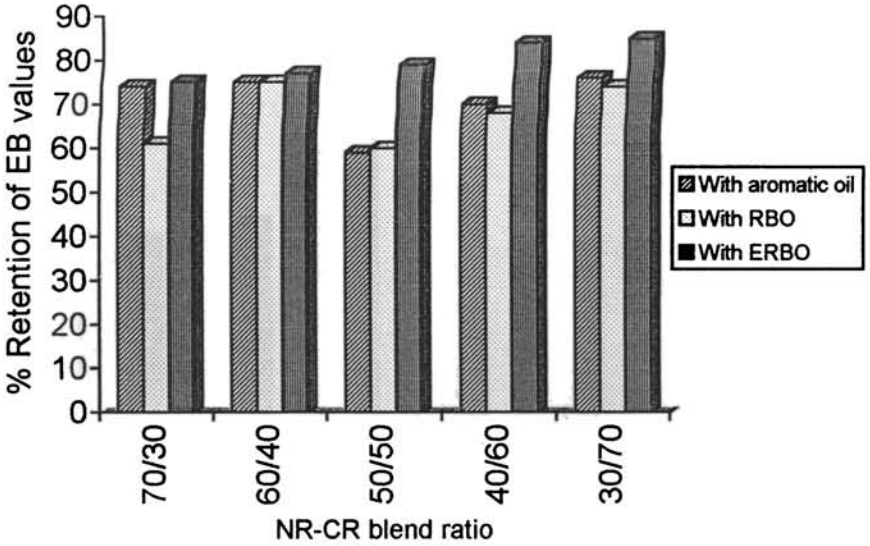

Fig. 4.11 Percentage retention of EB values with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

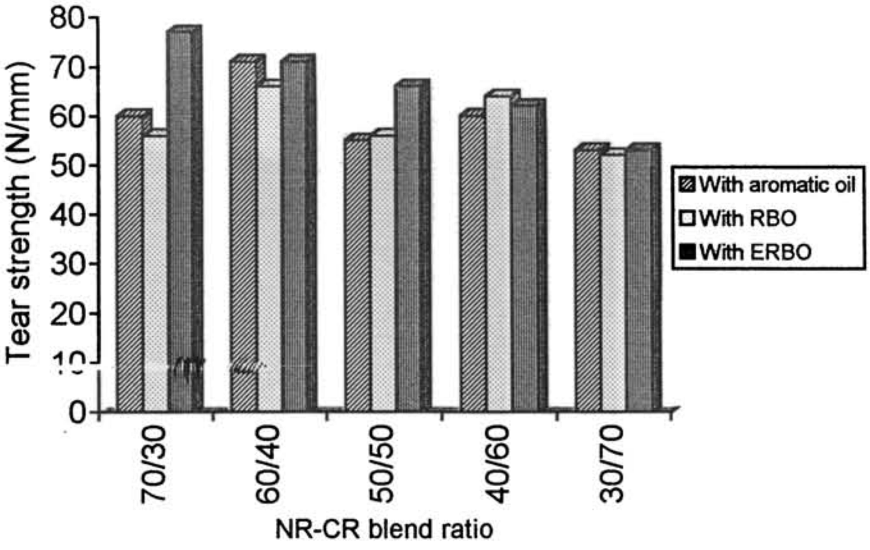

Fig. 4.12 Variation of tear strength with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

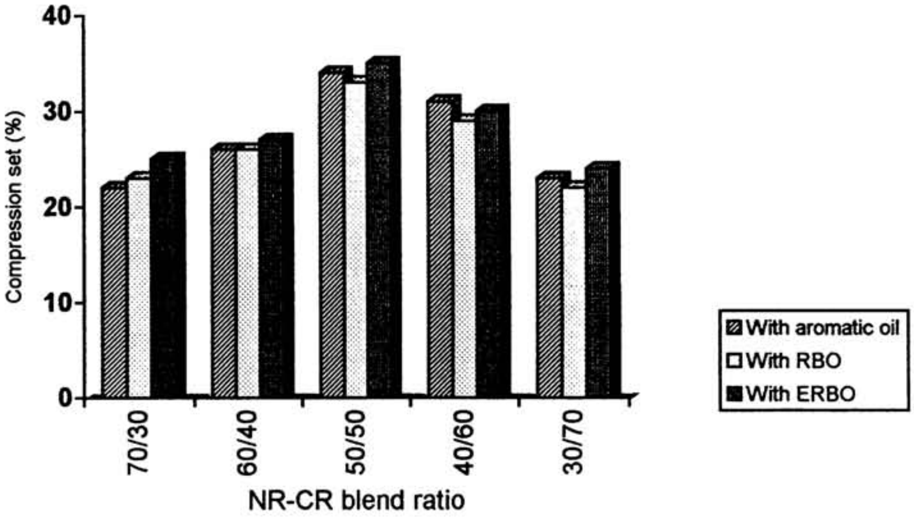

Fig. 4.13 Variation of compression set with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

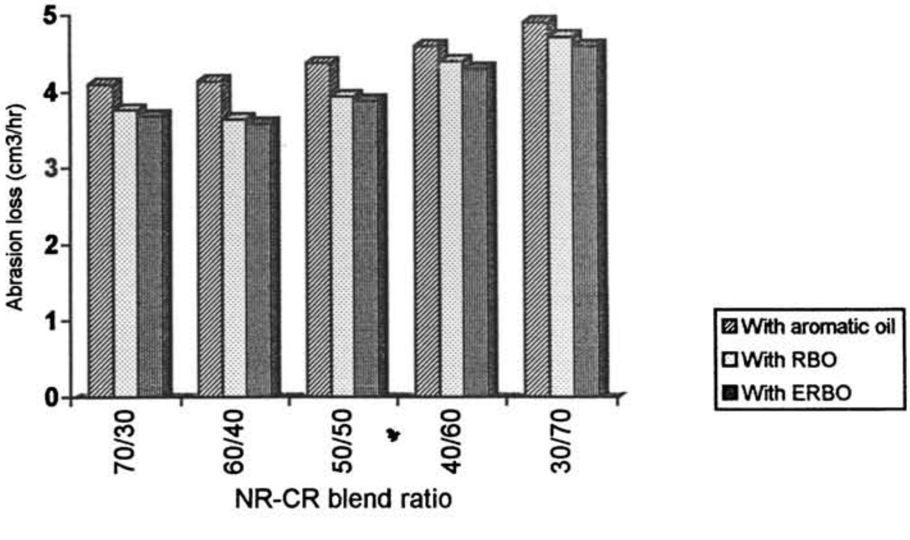

Fig. 4.14 Variation of abrasion loss values with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

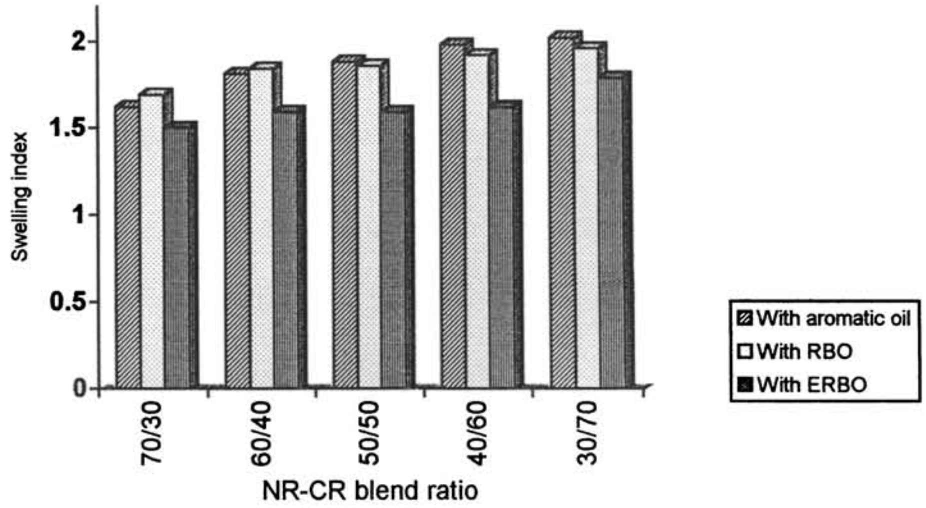

Fig. 4.15 Variation of swelling index with blend ratio of NR-CR blends prepared with aromatic oil/RBO/ERBO

CHAPTER V

Chapter V

USE OF RICE BRAN OIL AS PLASTICISER IN NBR-PVC BLENDS

The importance of plasticiser in the compounding of PVC could be appreciated only when we consider the fact that the usage of PVC was limited till the widespread use of plasticisers during 1930's, eventhough the discovery of PVC itself dates back to more than a century. Compared to elastomers, PVC which is a polymer with certain limitations like medium molecular weight, low crystallinity, poor heat stability above its softening point, low resistance to UV radiation and low softening point (70-75°C) found extensive application like other commodity plastics mainly due to the discovery of plasticisers and heat stabilizers. PVC resins are generally classified into suspension and emulsion grade depending on the techniques employed for their manufacture. Particles of suspension PVC are roughly spherical with diameter in the range of 50-250 micrometers. They have a porous internal structure with a significant volume of interstitial voids capable of absorbing plasticisers. Most resins used in the melt processing of plasticised PVC are of the suspension grade. More than 80% of PVC production accounts for this type of resin. However the emulsion polymer comprises small (<1 μm diameter) spherical particles. This type of resin can form plastisols when mixed with plasticisers at ambient temperature. There is no absorption of plasticisers by the primary particles which retain their integrity until the temperature is raised to cause fusion. Discovery of plasticisation of PVC by low molecular weight alkyl esters by B.F. Goodrich was of prime importance. In fact the plasticisation of PVC made it more akin to rubber than plastics. It was also found that most of the additives used in rubber industry like oils, waxes, stearates and metal oxides were also useful in PVC processing.

A brief discussion of role of plasticisers in PVC may be useful as the present study evaluates the role of RBO as a plasticiser in NBR-PVC blend. The proper choice of a plasticiser becomes an important part of PVC compounding. The efficiency of a plasticiser, otherwords the ability of a plasticiser in changing the properties of PVC to the desired extent with the use of as little plasticiser as possible is of paramount importance while selecting a plasticiser. In PVC industry this efficiency of a plasticiser is again a measure of how fast plasticisation takes place for a given grade. In general this depends on compatibility and molecular weight of the plasticiser. More compatible plasticisers are absorbed faster at a lower temperature compared to less compatible plasticisers for a given PVC sample. Now it has been well established that for the plasticiser molecules to be effective they must consist of sticky bits (to bind them to the polymer) and floppy bits (to separate polymer chains and allow movement.[1] In other words in order to be compatible with a polymer, a plasticiser needs to contain structural components which give loose reversible binding to the polymer; typically by dipole-dipole attraction. The remainder of the attached molecule, together with unattached molecules creates additional free volume in the structure which allows movement of the polymer chains and renders the material flexible. A simple model indicating favoured

polymer/plasticiser dipole alignments in plasticised PVC is shown in Fig.5.1.[2] Patel et al.[3] studied the effect of type and concentration of plasticiser on the behaviour of PVC,

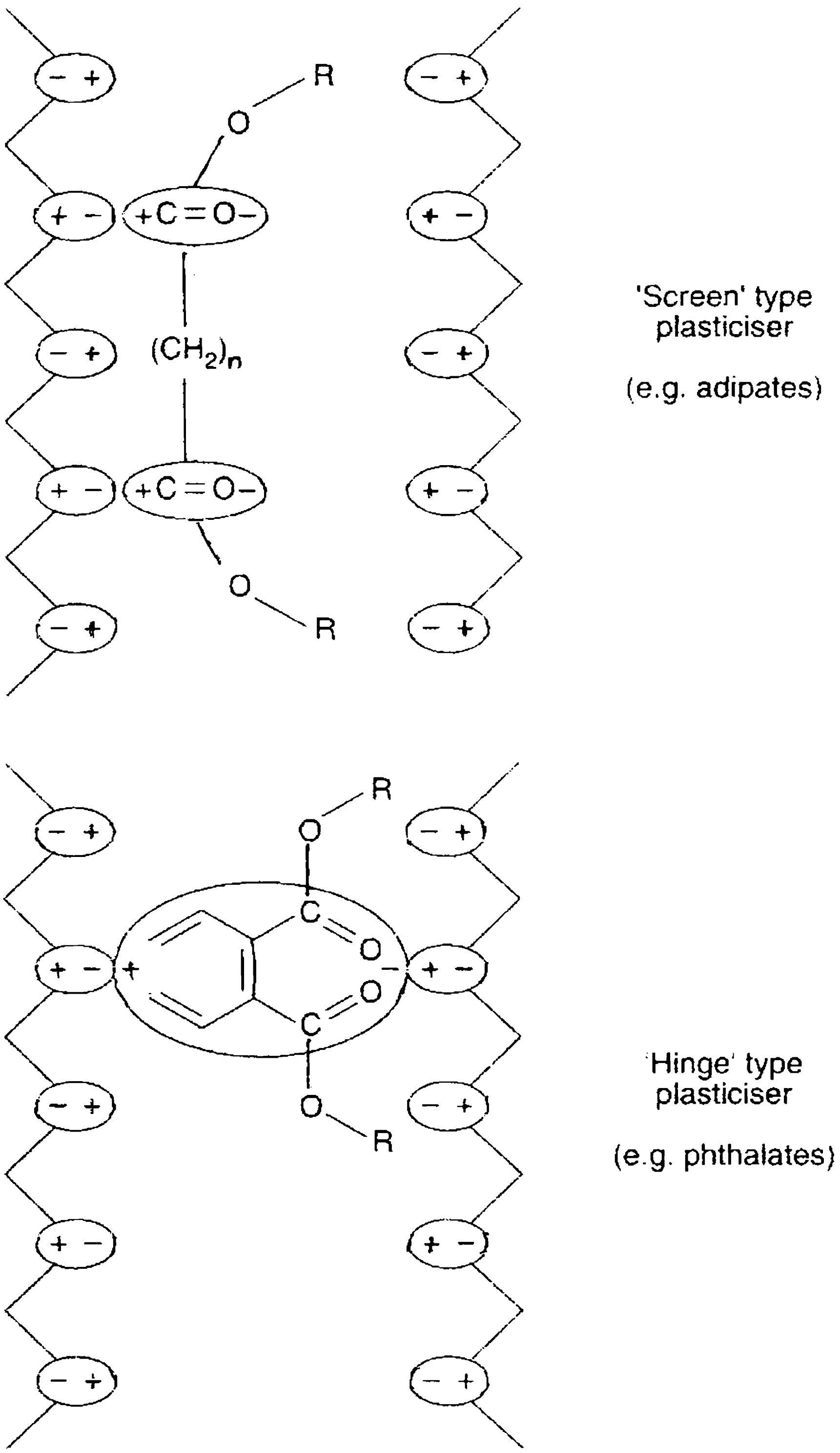

Fig. 5.1 Leuch's model of plasticisation

especially the fusion properties. More recently, access to molecular modelling computer programme and solid state nuclear magnetic resonance spectroscopy has given indications of the more complex interactions which are likely to occur in reality.[4]

Molecular mass, polarity and linearity of polymer molecules etc. are the most important molecular parameters that are to be considered while predicting performance of a particular plasticiser for use in PVC. Now it is almost clear that any compound with a molecular mass below 300 is likely to be too volatile for use in PVC and values above 800 causes low compatibility, and efficiency and hence difficult in processing. As far as the polarity aspect of the ester plasticiser molecule is concerned calculation of A_p/P_o ratio will give an indication of processability and compatibility. This ratio is equal to the number of carbon atoms present in the molecule (excluding aromatic carbon atoms) divided by the number of ester groups.[5] The aromatic carbon atoms are excluded from this calculation mainly due to the polarisable nature of aromatic groups which contributes to interaction. In this treatment, their effect is rated as neutral. As far as the linearity of the plasticiser molecule is concerned, if the structure is predominantly cyclic or branched, then the material will show poor low temperature performance. At an early stage, in the development of polymer technology the relationship between viscosity and plasticising performance was recognised by Leilich and this became known as Leilich's rate.[6] According to this rule the low viscosity indicates high softening efficiency, but at the cost of increasing tendency for rapid migration.

Lubricants also play an important role in PVC compounding. They are mainly used to reduce friction arising out of lack of ease of slippage of polymeric chains with respect to each other.. This friction can give rise to heat and hence the temperature of the melt increases, and hence can sometimes be detrimental to the stability, viscosity, colour etc. of the resin. The control of temperature to required level is an important requirement in PVC processing. Generally two different types of lubricants namely the internal and external types are used. The internal lubricants reduce the friction arising out of polymer chains whereas the external ones help to reduce friction between metal surface and the polymer chains in contact with it. However, there are certain class of lubricants which can perform dual roles and hence are called internal-external lubricants. Internal lubricants are quite compatible with PVC with the result that addition of these reduce internal friction, melt viscosity etc. giving better overall flow at lower power consumption. In this sense they are similar to plasticisers and often difficult to distinguish from them. It is a well known fact that plasticisation tends to decrease hardness and T_g, something which an internal lubricant also can do, though it has only limited compatibility with PVC. External lubricants have poor compatibility with PVC and hence tend to migrate towards surfaces thereby increasing lubricity between the melt and metal surface. Thus they have less effects on melt viscosity as compared to internal lubricants.

An ideal plasticiser is one which would show zero loss from the plasticised product and would remain chemically unchanged despite prolonged exposure to heat, light, aggressive chemicals, microorganisms and in contact with a wide variety of extracting media. Both thermodynamic and kinetic factors involve during a plasticiser loss from PVC. Thermodynamic factor covers the strength of interaction of the plasticiser with PVC relative to its compatibility with the medium into which it is migrating. In the case of volatile loss, vapour pressure is the measure of its compatibility with air. Kinetics deals with the rate at which the plasticiser diffuses to the surface of the PVC and the rate at which it migrates away from the surface into the adjacent medium. Again it is found that the loss will be increased by any factor which degrades plasticiser molecules into smaller fragments. These fragments will have lower PVC compatibility higher mobility and perhaps greater compatibility with extractants than with the plasticiser itself. There are many hostile factors which can remove the plasticiser from the polymer of which the compatibility limit factor of a plasticiser in the polymer is also to be taken into account. This factor may be defined as the level of incorporation of a plasticiser in PVC above which it will exude or sweat from the surface of a fully processed compound. For general purpose phthalates, phosphates etc. compatibility limits are far in excess of the levels which would need to be used in practice. However for others like chlorinated paraffins and some adipates compatibility limit places a real constraint to their use. Except fillers, plasticisers constitute the largest class of plastic additives both in terms of value and volume. Out of the total consumption of plasticisers world over approximately 90% is phthalates esters. DOP (dioctyl phthalate), DINP (di-isonoyl phthalate) and DIDP (di-isodecyl phthalate) constitute the three major general purpose PVC plasticisers. DOP is the largest single product used as a plasticiser throughout the world. In our study also the efficiency of RBO as plasticiser in NBR/PVC blend is compared to that of DOP. For ester type plasticisers it is the ester groups which provide compatibility with PVC whilst the size and shape of the remainder of the molecule dictates plasticising efficiency and permanence. It is reported that permeation of oxygen in PVC is increased with increasing

DOP content.[7] The glass transition temperature of PVC decreased and fractional free volume increased with increasing DOP content.

Miscibility of polymer blends was first observed with NBR-PVC system. In contrast to incompatible blends, blends of NBR-PVC show a single broad glass transition temperature (T_g) over a temperature range between T_g's of the unblended polymer.[8,9] However, studies of Matsuo et al[10] and Rovatti et al[11] have shown that NBR-PVC blends are not truly compatible in molecular level and confirmed the existence of distinct phases. It was also noted that blending of nitrile rubber with PVC significantly reduced, and in some cases eliminated, the loss of plasticiser due to volatilisation, migration or extraction.[12] This blend also exhibited inherent oil and fuel resistance and were suited for wide range of applications. The main worth of NBR to PVC compounds is as a nonextractable plasticiser. This is mainly due to the unique compatibility of PVC and NBR polymers. The presence of NBR in the blend also gives the final product a rubber look and feel.[13] It is also found that PVC forms a compatible blend with NBR in all proportions provided NBR has an acrylonitrile content of 25 to 40%. Lower or higher acrylonitrile content makes it incompatible with PVC.[14,15] Though NBR is not as efficient a plasticiser as DOP is, the former is used in the compounding of PVC due to its own inherent strength and ability to confer better mechanical properties to the blend. Because of the better mechanical properties of the blends they are widely being used in applications like wire and cable jacketing, gaskets, foot-ball covers, shoe uppers, tubing etc.[16] NBR also helps to retain any additional plasticiser like DOP or chlorinated paraffin added to PVC compounds. However NBR is not a good plasticiser as far as electrical resistance is concerned and hence the blend finds application only for making cable sheathing compounds and not for insulation compounds. In the NBR-PVC blend PVC has dual role, as a reinforcing filler and makes NBR resistant to ozone. In general, PVC is added to NBR when superior ozone resistance and ageing resistance is required. Poor processability and poor impact strength are the two major shortcomings of PVC. These shortcomings are tackled by mixing with plasticiser or by increasing processing temperature or by blending with NBR. This blending of NBR with PVC improves impact strength of the rigid PVC compositions and also increases the ozone resistance of vulcanisates.[17,18]

DOP being the largest tonnage plasticiser used in compounding of PVC, extensive toxicological studies were undertaken by different scientific organisations in UK and USA.[19] Results of studies conducted in USA in early 1980's indicated that substances like DOP and DOA (dioctyl adipate) are harmful to human beings and are carcinogenic.[20] But later studies absolved these substances from its carcinogenic potential.[21] Apart from the toxic nature, these chemical substances, can also contribute to the environmental pollution as they can migrate from PVC compounds. Under this backdrop it will be worthwhile if some of the chemical plasticisers like DOP traditionally being used in PVC or its blends could be replaced by an ecofriendly and nontoxic substance like RBO.

In the present study a natural product viz., rice bran oil is used in place of chemical plasticiser like DOP conventionally used for the preparation of NBR-PVC blends. The effect of replacement of DOP by RBO in the blends was investigated by compairing the processability, cure characteristics, physical and mechanical properties of respective vulcanisates from the blends. In order to ascertain the behaviour of the oil in the blend in presence of fillers, blends were prepared in different blend ratios with carbon black/silica using RBO and their properties were compared to those prepared with DOP.

EXPERIMENTAL

NBR and PVC having specifications given in chapter II were used in the present investigation. Zinc oxide, magnesium oxide, stearic acid, mercaptobenzothiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, carbon black (HAF 330), silica, dioctyl phthalate used are all of commercial grade. Stabiliser system consisting of ZnO, MgO and stearic acid was used for PVC. The resin was first thoroughly mixed with stabilizers and then plasticiser DOP/RBO was added with thorough mixing so as to get the ingredients uniformly mixed. Blends of NBR and PVC were then prepared in a Brabender plasticorder, model PL-3S. The mixing head was heated to 150°C and the rotor speed was adjusted to 50 rpm. Mill masticated NBR was first added to mixing chamber and allowed to heat up and homogenise for one minute. PVC compound was then added over a period of 5 minutes and mixing was continued for 2 more minutes till a constant torque is recorded in the torque rheometer. The final compounding of the blends prepared in different blend ratios using fillers and DOP/RBO was done in a laboratory model two-roll mixing mill at a temperature of 80°C as per the formulation given in Tables 5.2, 5.3 and 5.4. The amount of curatives used in the blend was selected on the basis of weight percentage of NBR in the blend. When black was used as the filler 4 phr of DOP/RBO was used as processing aid and for silica 6 phr processing aid was required. These quantities of oils were selected based on the results obtained on our earlier studies of NBR processability using DOP/RBO as mentioned in Chapter III. The final compound so prepared was kept for maturation at 27°C for a period of 24 hrs.

When silica is used as a filler in rubber compounds acidic silanols or hydroxyl groups on the surface of the filler can interact with basic accelerators. This usually results in unacceptable long cure times and slow cure rates. In order to normalise the cure rate, diethylene glycol (DEG) is usually included in the compound preparation. In our study also 1.5 phr diethylene glycol was used for the preparation of silica filled blends.

The cure characteristics of the compounds were determined at 160°C on a Geottfert elastograph model 67.85. The cure data reported are the following: Optimum cure time is the time taken for attaining 90% of the maximum torque. Elastographic scorch is calculated as the time for 10% of vulcanisation. Cure rate index was determined from the cure curves of the respective mixes as $100/t_{90}$-t_{10}, where t_{90} and t_{10} are times corresponding to the optimum cure and ten percent vulcanisation respectively. The maximum - minimum torque (MH_F – ML) of each mix was also calculated. The compounds were vulcanised upto their optimum cure time in an electrically heated laboratory type hydraulic press at 160°C and at a pressure of 11.764 MPa. The tensile properties of the vulcanisate were determined on a Zwick universal testing machine using a crosshead speed of 500 mm/min. as per ASTM designation D 412-87 (method A). Dumbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Heat ageing was carried out at 100°C for 96h in an air oven. Tear resistance is tested as per ASTM designation D 624-86 using angular test pieces.

Table 5.1 Formulation of PVC Compound

Ingredients	Phr
Poly (vinyl chloride)	100
ZnO	4
MgO	4
Stearic acid	2
DOP/RBO	20

Table 5.2 Formulation of NBR in the unfilled blend

Ingredients	Phr
NBR	100
Sulphur	1.5
ZnO	3.0
Styrenated phenol	2.0
Stearic acid	1.0
MBTS	1.5
TMTD	0.5

Table 5.3 Formulation of NBR in the black filled blend

Ingredients	Phr
NBR	100
Sulphur	1.5
ZnO	3.0
Stearic acid	1.0
Styrenated phenol	2.0
MBTS	1.5
TMTD	0.5
Carbon black (HAF 330)	40.0
DOP/RBO	4.0

Table 5.4 Formulation of NBR in silica filled blend

Ingredients	Phr
NBR	100
Sulphur	1.5
ZnO	3.0
Stearic acid	1.0
Styrenated phenol	2.0
Precipitated silica	60.0
Diethylene glycol	1.5
MBTS	1.5
TMTD	0.5
DOP/RBO	6.0

Compression set was tested as per ASTM D 395-86 (method B). Abrasion resistance was evaluated using DIN abrader (DIN 53516). The swelling index of the different samples was determined by immersing 0.2g of the sample in chloroform for 24hr. All these experiments are described in detail in chapter II.

The processability study of NBR-PVC blend using DOP/RBO was carried out in a Brabender plasticorder. For the present study the temperature of the test chamber was kept at 150°C, and the speed of the roller mixing heads in the plasticorder was kept initially at 50 rpm. The weight of NBR, PVC and other ingredients were so selected as to keep the total weight of the blend 40 gm for each blend ratio. First NBR was passed six times in a two-roll mill at a nip gap of 0.8 mm to get a thin sheet. This was cut into small strips before feeding into the plasticorder. The total mixing time was kept at 8 minutes with the following break-up. NBR was allowed to heat up and homogenise for one minute, then PVC resin premixed with ZnO, MgO, stearic acid, and DOP/RBO was added over a period of 5 minutes, and the mixing was allowed to continue for two more minutes. The final torque reading in the torque rheometer was recorded. The experiment was repeated using different levels of DOP/RBO (15/20/25 phr) at different rpm (50, 70 and 90) in two different blend ratios (50/50 and 70/30). Viscosity (torque/rpm) of the blend in each blend ratios is plotted against rpm for different levels of oil used. The corresponding flow curves are shown in Figs.5.2 and 5.3.

RESULTS AND DISCUSSION

Processability

The optimum quantity of DOP/RBO required for the blend preparation was determined by using different levels of DOP/RBO during the preparation of the blend in the Brabender plasticorder. For 50/50 and 70/30 NBR-PVC blend 15, 20 and 25 phr levels of DOP/RBO were tried. From the flow curves shown in Figs.5.2 and 5.3 it is clear that the maximum torque obtained in 50/50 and 70/30 NBR-PVC blends during mixing at 150°C and at 50 rpm is well within 30 Nm range. It may also be noted that a near absence of any white patches (due to unfused PVC particles) on the surface of the thin sheet made out of the DOP/RBO based blend by passing through a two roll mill at a nip gap of 0.8 nm can be considered as indication of the uniformity of the blend. Here 20 phr DOP/RBO (for 100 phr PVC) is taken as the optimum level of the plasticiser for the preparation of the blend as this amount was found to be enough for the preparation of a uniformly mixed blend.

The same loading of rice bran oil produced less torque values compared to DOP and this is seen reflected in the lower viscosity (torque/rpm) of the blends prepared with RBO. This lower viscosity of the blends prepared with RBO may be attributed to the ability of RBO to function as an external lubricant also in the blend. From the flow curves for the blends under review, it is clear that both the systems are pseudoplastic as seen from the decrease in viscosity with increase in rpm. When the level of RBO is increased above 25 phr the preparation of the blend was found to be difficult as the torque developed was too small to get a uniformily mixed blend within the stipulated period. From the flow

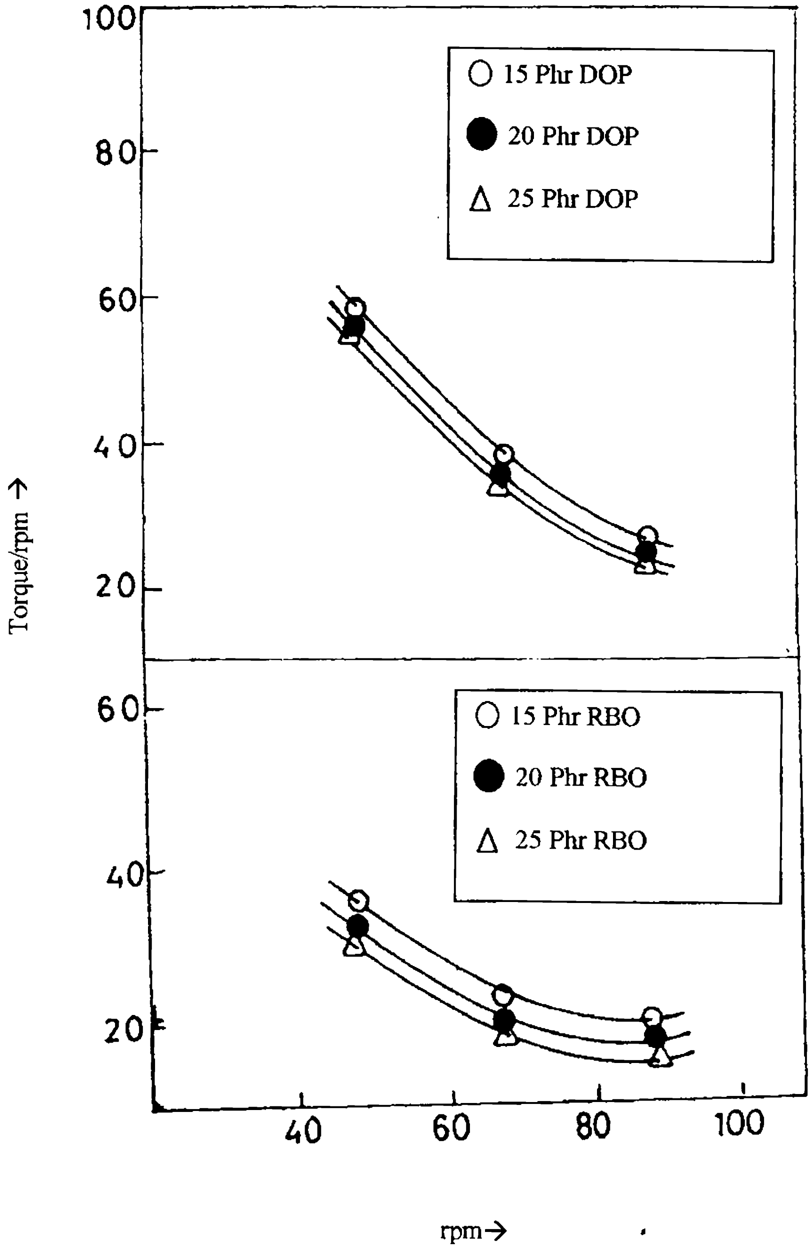

Figure 5.2 Flow curves of 50/50 NBR-PVC prepared at 150°C with DOP/ RBO

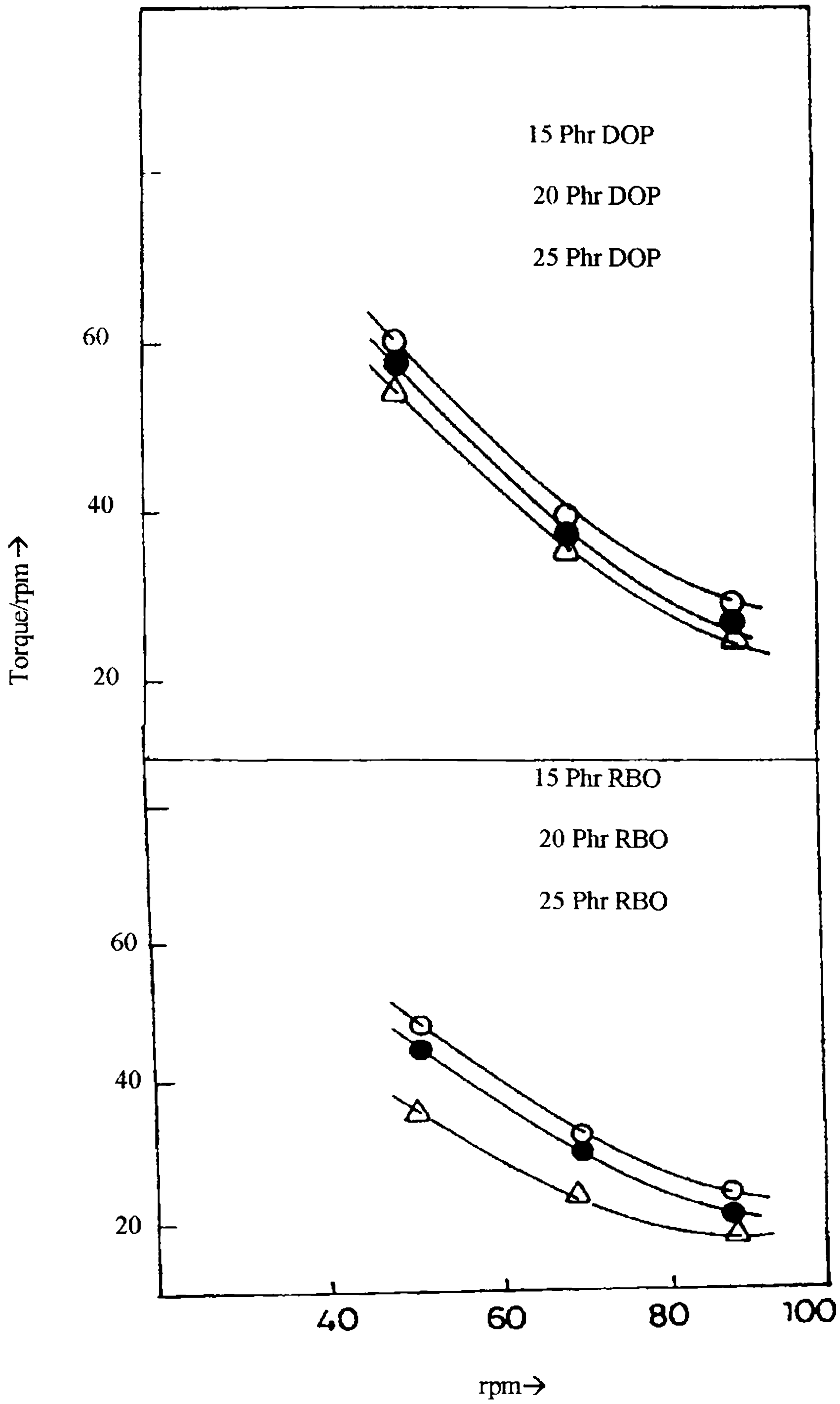

Figure 5.3 Flow curves of 70/30 NBR-PVC prepared at 150°C with DOP/ RBO

curves it is clear that in both 50/50 and 70/30 NBR-PVC blends, 20 phr of DOP/RBO, on weight basis is sufficient for making a proper blend at the blending temperature of 150°C.

Based on the processability studies the experimental blends are prepared using 20 phr RBO and their cure characteristics, physical and mechanical properties are compared with the corresponding blends prepared with DOP. These results are reported in the subsequent section. From the processability study it is evident that DOP could be replaced with RBO for the preparation of the blend; the main advantage of RBO over DOP being that RBO offers lesser Brabender torque compared to DOP. This aspect will have technological and economic advantage during the preparation of the blend.

Cure characteristics

The cure characteristics of the blends prepared with RBO in different blend ratios with and without filler and the corresponding control compounds prepared with DOP were evaluated using Goettfert elastograph at 160°C. The cure curves of the blends prepared with DOP are given in Figs.5.4, 5.5 and 5.6 and those with RBO are given in Figs.5.7, 5.8 and 5.9. From the figures it is evident that the maximum torque developed for all the blends prepared with DOP is higher compared to the ones prepared with RBO. This is in accordance with the processing properties discussed in the earlier section. The reason for this observation may be attributed to the better compatibility or lower plasticizing nature of DOP over RBO. This observation is equally true for the blends prepared with different fillers also. From the figures it is also evident that the blends under review do not show any reversion characteristics irrespective of the nature of plasticisers and fillers used. The cure characteristics of the blends with and without fillers prepared with DOP are given in Table 5.5, 5.7 and 5.9 and of the corresponding blends prepared with RBO are given in Tables 5.6, 5.8 and 5.10. From the cure time values of the different blends prepared with DOP/RBO it is clear that the incorporation of RBO in the blend gives a favourable effect as seen by increased cure rate in these mixes. This is especially so for the black filled blends prepared with RBO. This trend is also shown by silica filled blends prepared with RBO. This cure accelerating nature of the RBO may be due to the presence of various kinds of free fatty acids present in the oil. The lower cure time and scorch time values of the silica based blends prepared with RBO has got special significance, as silica has traditionally been known for its cure retarding properties.[22] It is a known fact that accelerator systems are deactivated by silica. However the scorch time values (a measure of processing safety) is higher for blends prepared with DOP compared to RBO and is true for both filled and unfilled systems. The fact that incorporation of RBO in these blends in place of DOP, significantly reduce cure time values can have definite technological advantages.

Crosslink density

The swelling index of the blend prepared with DOP/RBO were determined using chloroform as the solvent. These swelling index values are a measure of crosslink density as it is inversely proportional to the crosslink density. From Fig.5.18 it is clear that the blends prepared with DOP show lower swelling value and hence higher crosslink density as compared to the ones prepared with RBO. This trend is shown by filled blends prepared with DOP also. The greater compatibility of DOP over RBO towards the blend may be

Table 5.5 Cure characteristics of unfilled NBR-PVC blends with DOP

	Blend ratio				
	50/50	60/40	70/30	80/20	90/10
Maximum torque MH_F(Nm)	0.121	0.198	0.208	0.224	0.236
Minimum torque ML (Nm)	0.013	0.018	0.016	0.014	0.014
(MH_F – ML) torque (Nm)	0.108	0.180	0.192	0.210	0.222
Optimum cure time t_{90} (min)	7.6	7.4	5.8	5.2	3.9
Elastographic scorch time t_{10} (min)	2.0	1.8	1.9	1.8	1.8
Cure rate index	18	18	26	30	48

Table 5.6 Cure characteristics of unfilled NBR-PVC blends with RBO

	Blend ratio				
	50/50	60/40	70/30	80/20	90/10
Maximum torque MH_F (Nm)	0.117	0.145	0.140	0.138	0.150
Minimum torque ML (Nm)	0.020	0.014	0.016	0.014	0.012
(MH_F – ML) torque(Nm)	0.097	0.131	0.124	0.124	0.138
Optimum cure time t_{90}(min)	6.9	5.5	5.2	4.7	2.6
Elastographic scorch time t_{10} (min)	1.6	1.6	1.7	1.7	1.8
Cure rate index	18.8	25.6	28.6	33.3	125

Table 5.7 Cure characteristics of black filled NBR-PVC blends with DOP

	Blend ratio				
	50/50	60/40	70/30	80/20	90/10
Maximum torque MH$_F$ (Nm)	0.139	0.207	0.218	0.280	0.301
Minimum torque ML (Nm)	0.069	0.060	0.060	0.060	0.050
(MH$_F$ – ML) torque (Nm)	0.070	0.147	0.158	0.220	0.251
Optimum cure time t_{90} (min)	12.5	6.2	5.5	4.9	2.7
Elastographic scorch time t_{10} (min)	1.9	1.7	1.7	1.7	1.5
Cure rate index	9.43	22.0	26.0	31.0	83.0

Table 5.8 Cure characteristics of black filled NBR-PVC blends with RBO

	Blend ratio				
	50/50	60/40	70/30	80/20	90/10
Maximum torque MH$_F$ (Nm)	0.134	0.174	0.189	0.279	0.270
Minimum torque ML (Nm)	0.065	0.070	0.070	0.080	0.080
(MH$_F$ – ML) torque (Nm)	0.069	0.104	0.119	0.199	0.190
Optimum cure time t_{90} (min)	3.1	3.1	2.9	2.8	1.5
Elastographic scorch time t_{10} (min)	1.6	1.7	1.7	1.7	1.1
Cure rate index	66.6	71.4	83.3	90.9	250

Table 5.9 Cure characteristics of silica filled NBR-PVC blends with DOP

	Blend ratio				
	50/50	60/40	70/30	80/20	90/10
Maximum torque MH$_F$ (Nm)	0.267	0.279	0.434	1.010	1.080
Minimum torque ML (Nm)	0.174	0.185	0.200	0.200	0.220
(MH$_F$ – ML) torque (Nm)	0.093	0.094	0.234	0.810	0.860
Optimum cure time t_{90} (min)	12.2	6.6	5.4	3.6	2.8
Elastographic scorch time t_{10} (min)	2.3	1.9	1.3	1.1	1.0
Cure rate index	10.1	21.2	24.4	40.0	55.6

Table 5.10 Cure characteristics of silica filled NBR-PVC blends with RBO

	Blend ratio				
	50/50	60/40	70/30	80/20	90/10
Maximum torque MH$_F$(Nm)	0.195	0.270	0.420	0.730	1.070
Minimum torque ML(Nm)	0.113	0.167	0.200	0.200	0.210
(MH$_F$ – ML) torque(Nm)	0.082	0.103	0.220	0.530	0.860
Optimum cure time t_{90}(min)	5.8	4.6	2.5	1.9	1.9
Elastographic scorch time t_{10} (min)	1.6	1.6	1.2	1.0	1.0
Cure rate index	23.8	33.3	76.9	111.1	111.1

cited as the reason for this observation. This observation is further supported by the fact that MH_F-ML (maximum torque — minimum torque) of the different blends with and without fillers using DOP (Refer Tables 5.5, 5.6, 5.7, 5.8, 5.9 and 5.10) are higher than those of the corresponding ones prepared with RBO. It is also reported that MH_F-ML is a direct function of crosslink density.[23] From these observations it may be concluded that better crosslinking in the blend is achieved when DOP is used in the blend compared to RBO.

Tensile properties

The variation in tensile properties before and after ageing of the blend vulcanisates with and without fillers are represented in Figs.5.10 and 5.11. From the figures it is clear that in the case of unfilled blend the tensile strength values are higher for the ones prepared with DOP. This is evident from the higher crosslink density of these blends. But as the weight percentage of PVC in the blend decreases tensile values also get decreased. For the black filled blends except for 50/50 blend both DOP and RBO based blends showed more or less same tensile values. For silica filled blends the tensile values are more or less same for the 50/50 blend. However as the weight percentage of rubber in the blend increases, the blends prepared with DOP showed better tensile values.

The elongation at break values of the different blend vulcanisates are given in Fig.5.12. From the figure it is clear that the elongation at break values are slightly higher for the unfilled blends prepared with DOP. This is equally true for silica filled blends also. The modulus at 200% (Fig.5.13) is also slightly higher for the unfilled and silica filled blends prepared with DOP, which again is indicated by the higher crosslink density of the vulcanisates from these blends. After ageing the different vulcanisates at 100°C for 96hr, it is found that the percentage retention of tensile values are more for unfilled and black filled blends prepared with DOP compared to RBO. However a reverse trend is noted for the silica filled blends. (Fig. 5.14).

Tear strength, compression set and abrasion resistance are the other physical properties studied for the different systems under review. These values are given in Figs.5.15, 5.16 and 5.17. It is clear from the figures that the tear values are decreasing as the weight percentage of PVC in the blend decreases irrespective of the nature of the plasticiser used. This is a clear indication of the better tear strength afforded by PVC to the blend both in the filled and unfilled systems. It may also be noted that with few exceptions the tear strength values of the different vulcanisates prepared with DOP are slightly higher compared to the ones prepared with RBO. It may also be attributed to the greater compatibility of DOP over RBO towards the blend. A notable feature of the blends prepared with RBO is the better abrasion resistance values of these vulcanisates compared to the corresponding ones prepared with control (Fig.5.17). This may be ascribed to the lower stiffness of the blend vulcanisate prepared with RBO. The compression set values are more or less same for all the blends prepared with DOP and RBO (Fig.5.16). However the compression set values are decreasing as the weight percentage of PVC in the blend decreases. This may be due to the greater rubber chain flexibility brought about by the decreasing amount of PVC in the blend.

Conclusions

1. From the processability studies it is obvious that the incorporation of RBO in the blend has beneficial effect as the torque generated is found to be significantly less compared to the control blends based on DOP.

2. The cure characteristics of the blends prepared with RBO suggest that RBO has cure accelerating property (higher cure rate values) compared to the ones prepared with DOP. The lower cure time values has a direct bearing on the processing operations with definite technological advantage.

3. A comparison of the mechanical properties of the blends prepared with DOP and RBO indicate that the replacement of DOP by RBO does not affect the physical and mechanical properties of the blends significantly eventhough DOP is found to be slightly superior in some of the physical properties estimated. The high abrasion resistance of the blends prepared with RBO may be considered as a beneficial feature.

4. It may be concluded that replacement of DOP with RBO in the blend is advantageous as RBO is available comparatively cheap in India. Apart from these, RBO which is a nontoxic and ecofriendly natural product, could be recommended as a plasticiser substitute for DOP in NBR-PVC blends.

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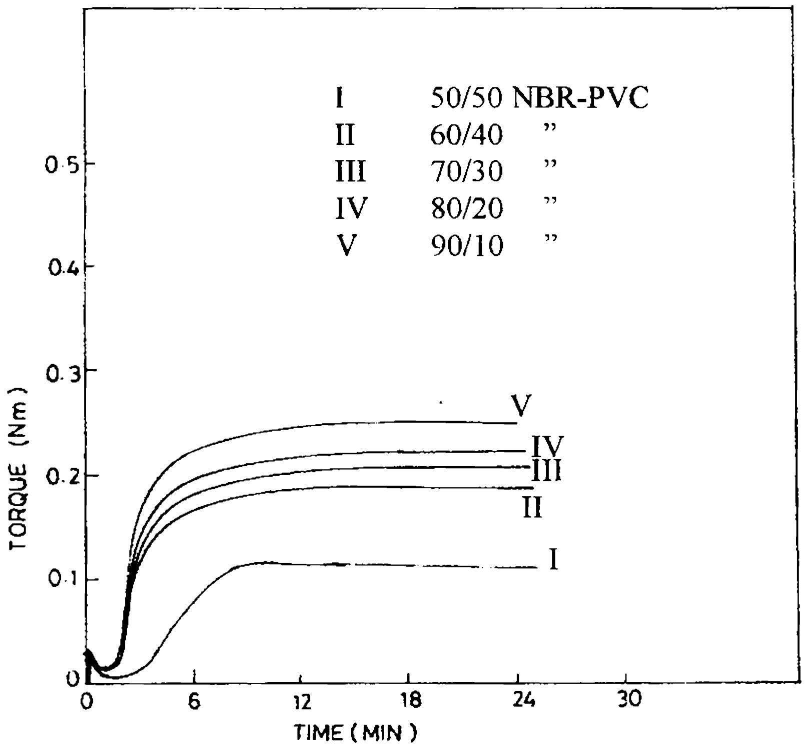


Figure 5.4 Cure curves of NBR – PVC with DOP

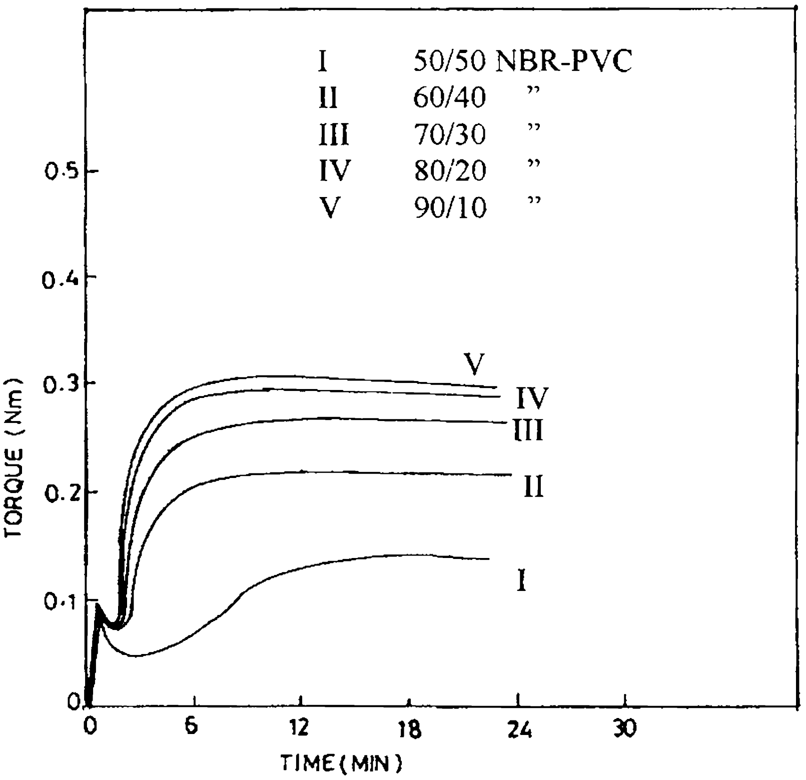


Figure 5.5 Cure curves of black filled NBR – PVC with DOP

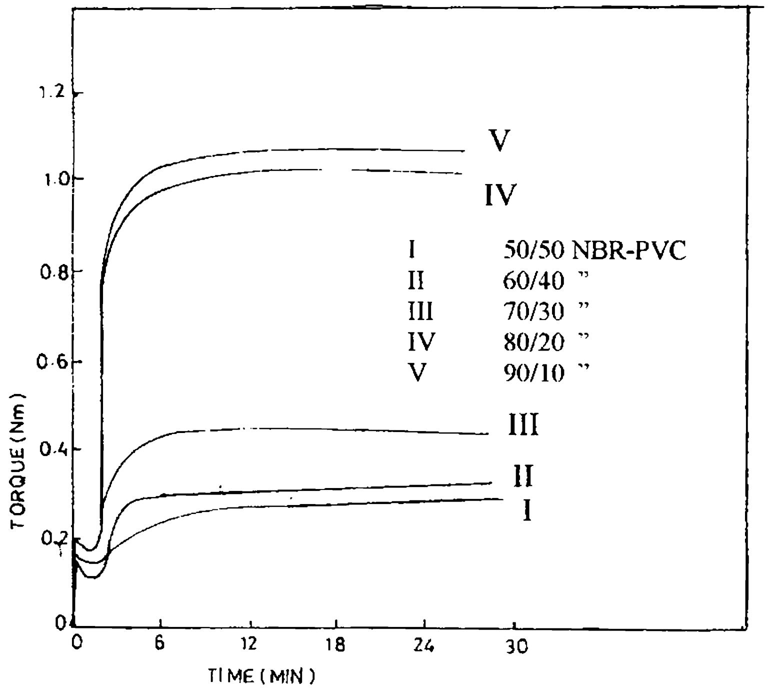


Fig. 5.6 Cure curves of silica filled NBR-PVC with DOP

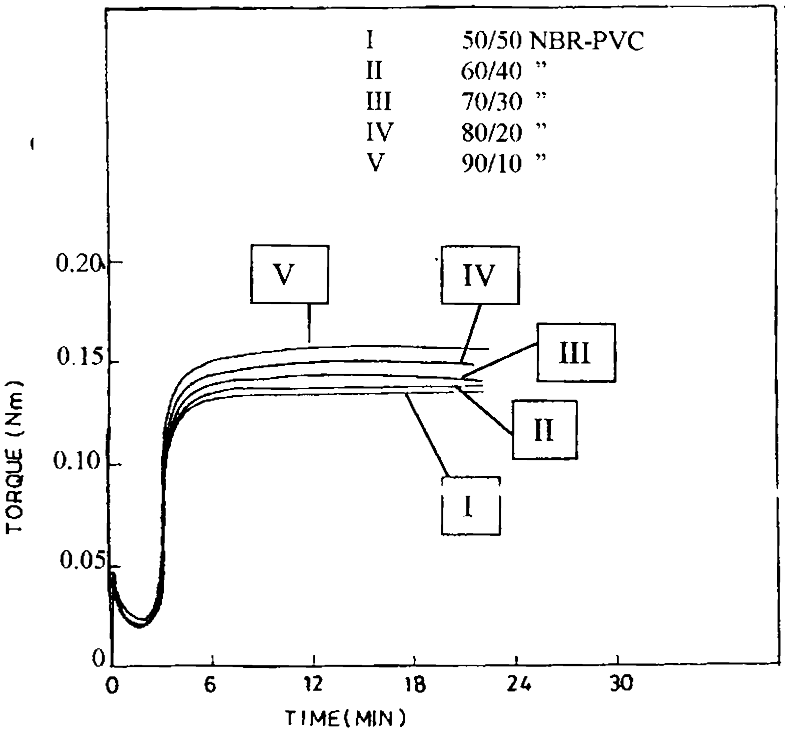


Fig. 5.7 Cure curves of NBR – PVC with RBO

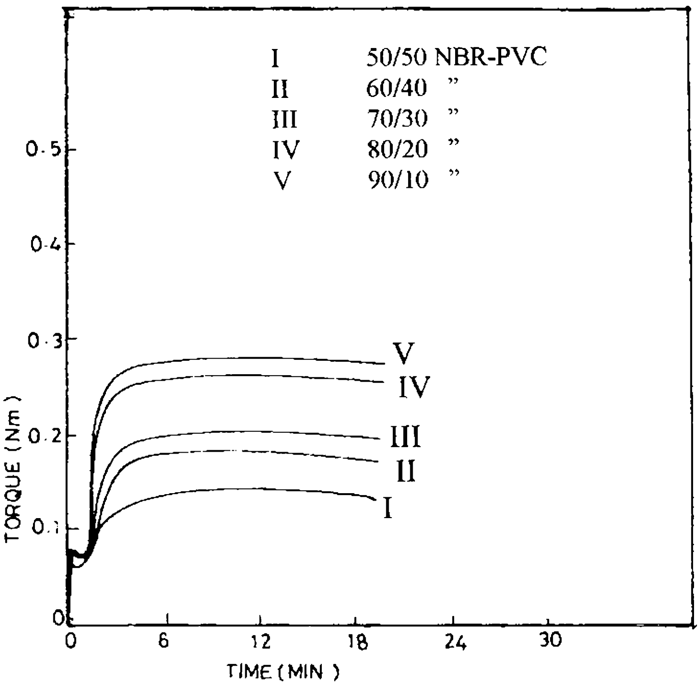


Fig. 5.8 Cure curves of black filled NBR-PVC with RBO

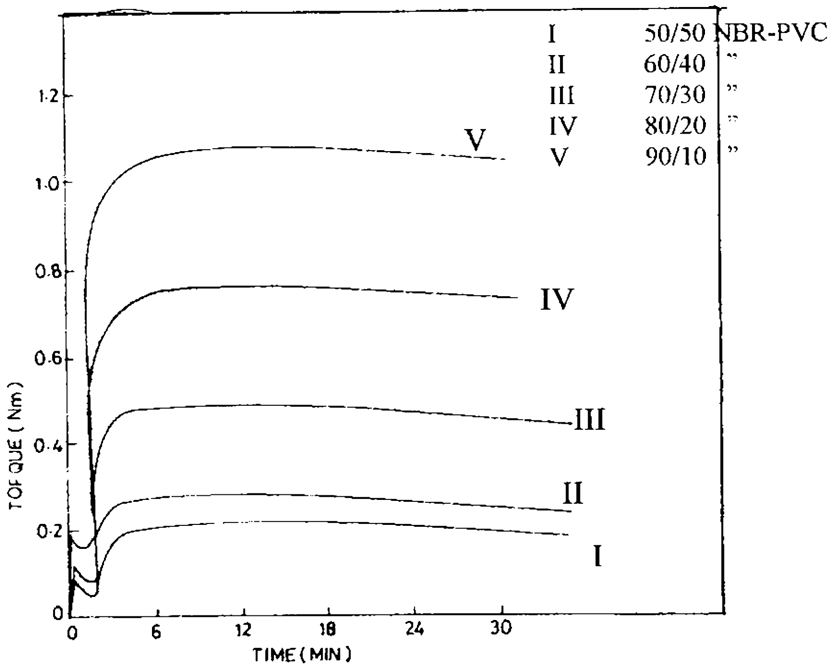


Fig. 5.9 Cure curves of silica filled NBR-PVC with RBO

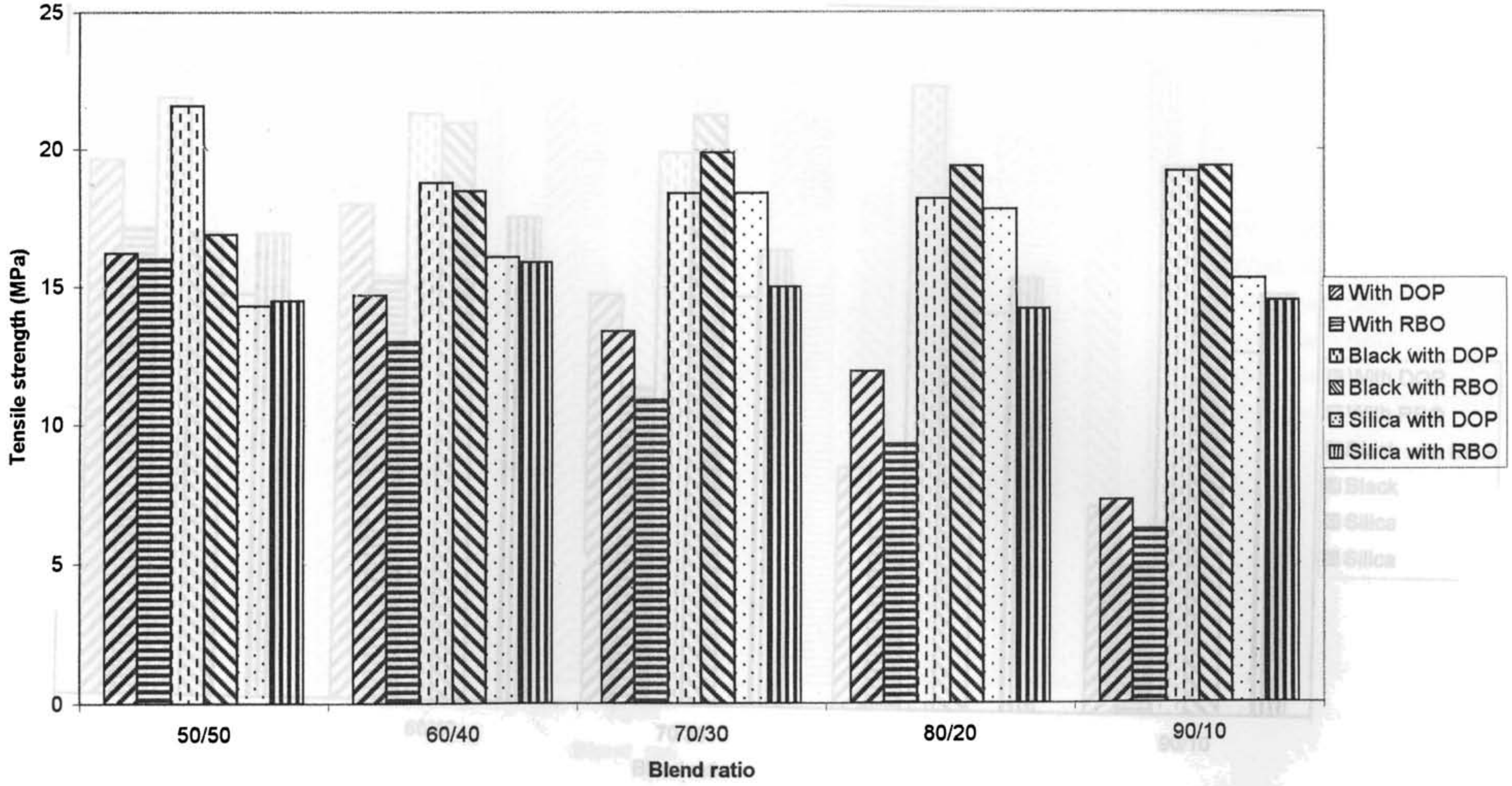


Fig. 5.10 Variation of tensile strength of balck/silica/unfilled NBR-PVC blends prepared with DOP/RBO

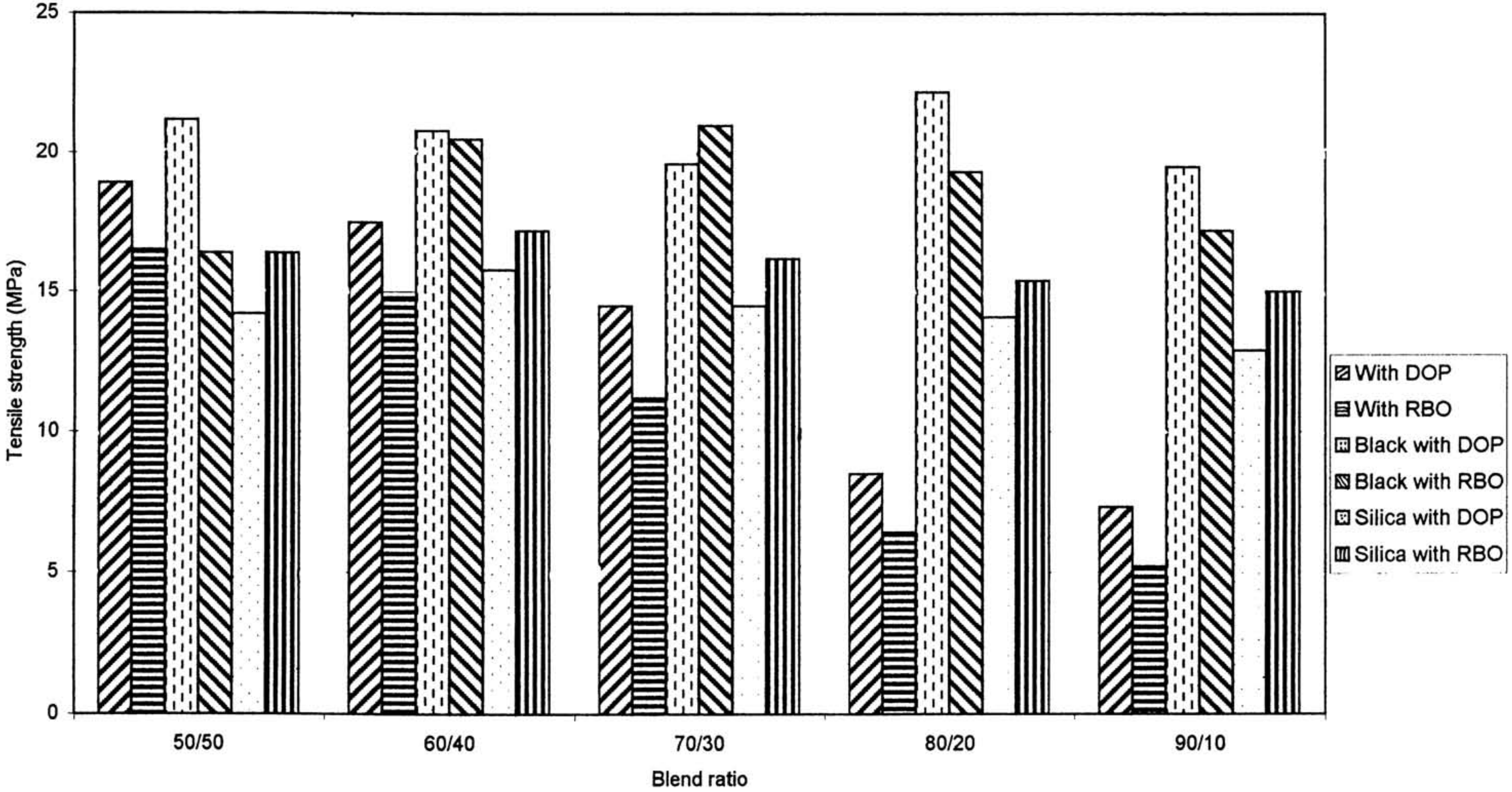


Fig 5.11 Variation of tensile strength (after ageing) of black/silica/unfilled NBR-PVC blends with DOP/RBO

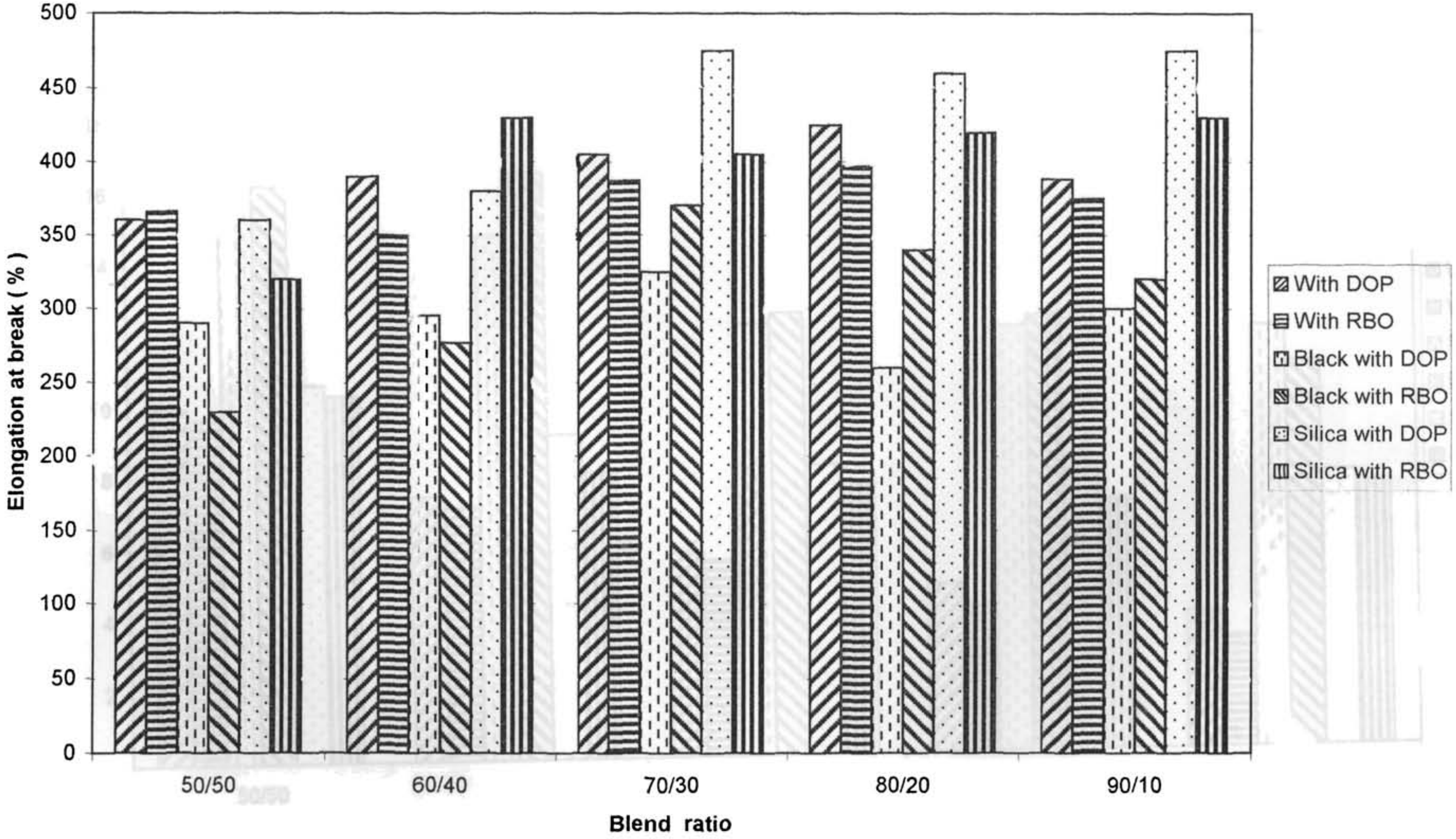


Fig 5.12 Variation of elongation at break of black/silica/unfilled NBR-PVC blends prepared with DOP/RBO

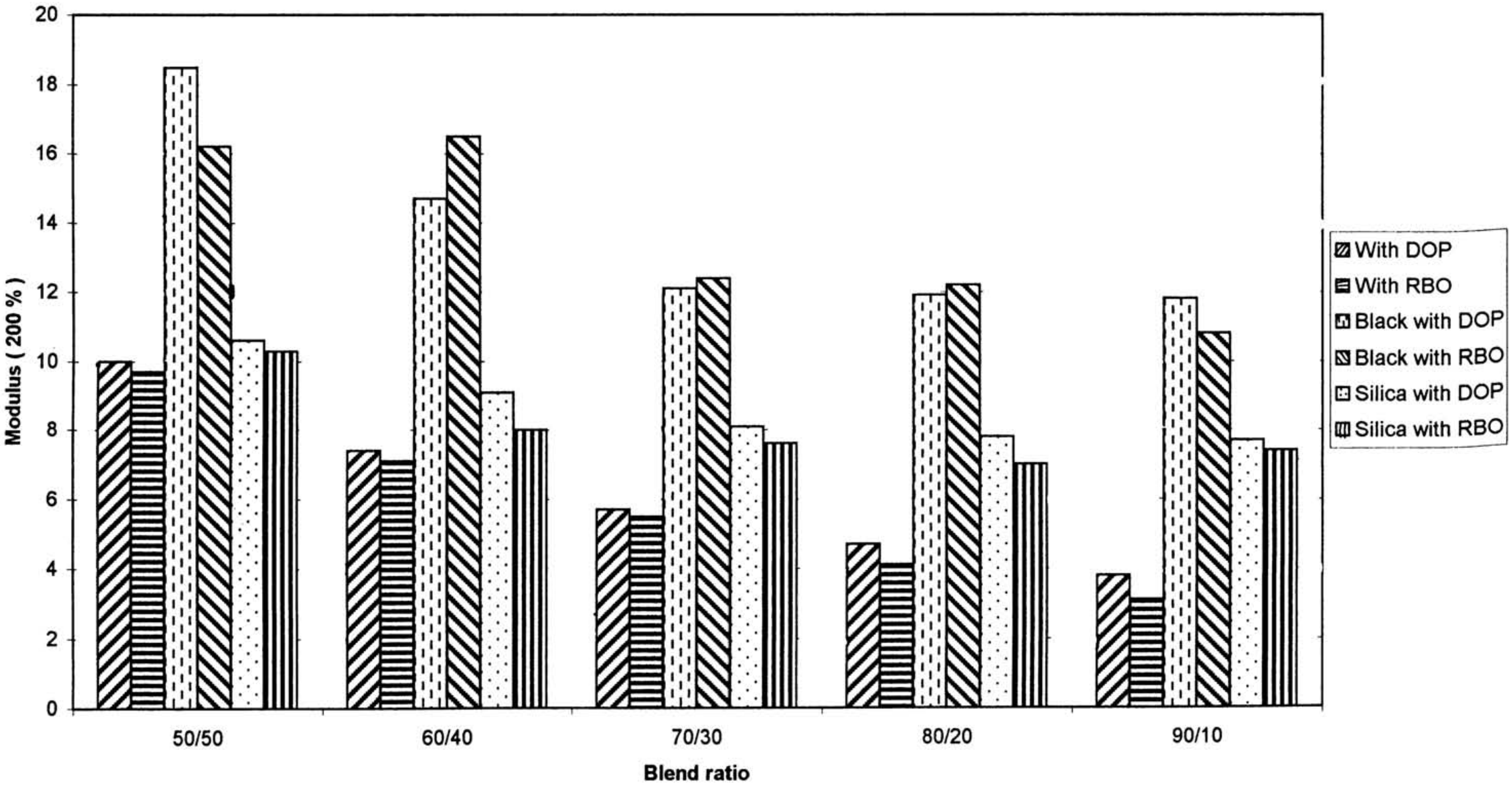


Fig 5.13 Variation of 200 % modulus of black/silica/unfilled NBR-PVC blends prepared with DOP/RBO

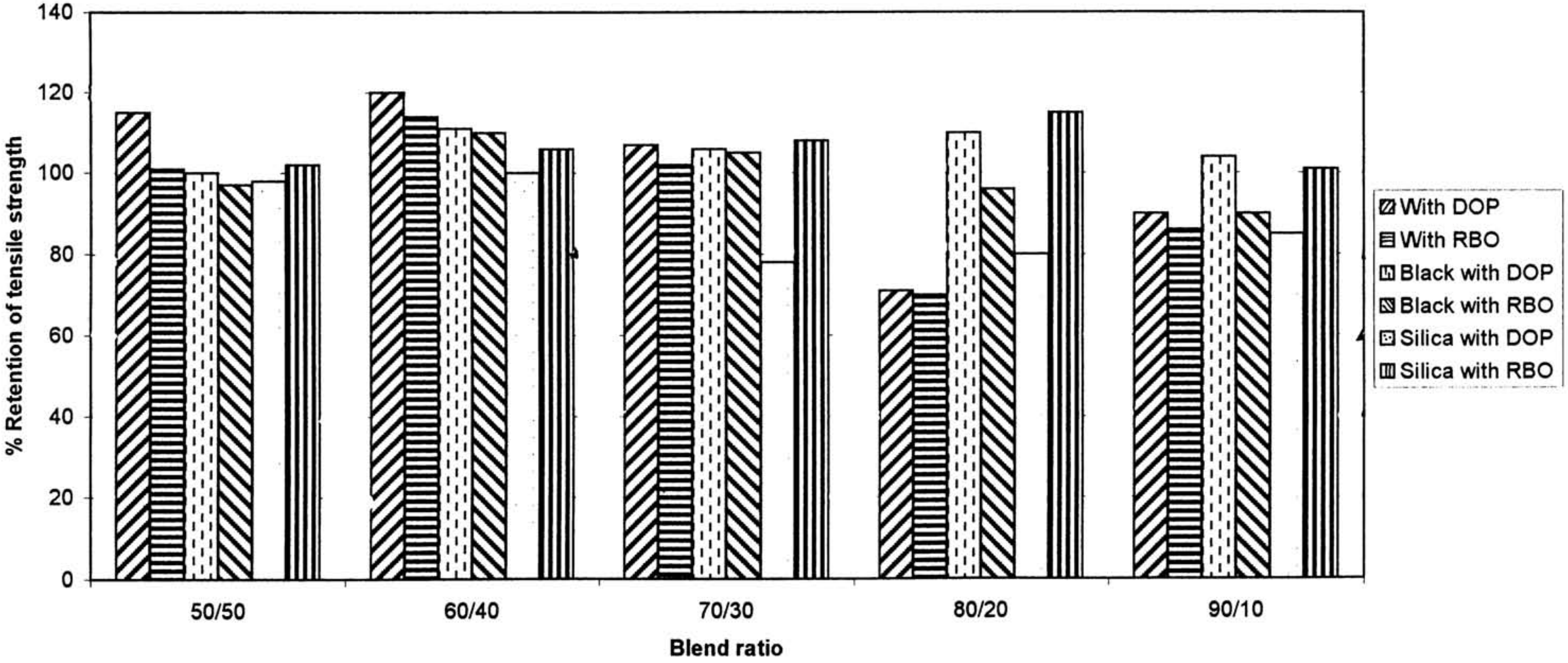


Fig 5.14 Variation of % retention of tensile strength with blend ratio of black/silica/unfilled NBP-PVC blends prepared with DOP/RBO

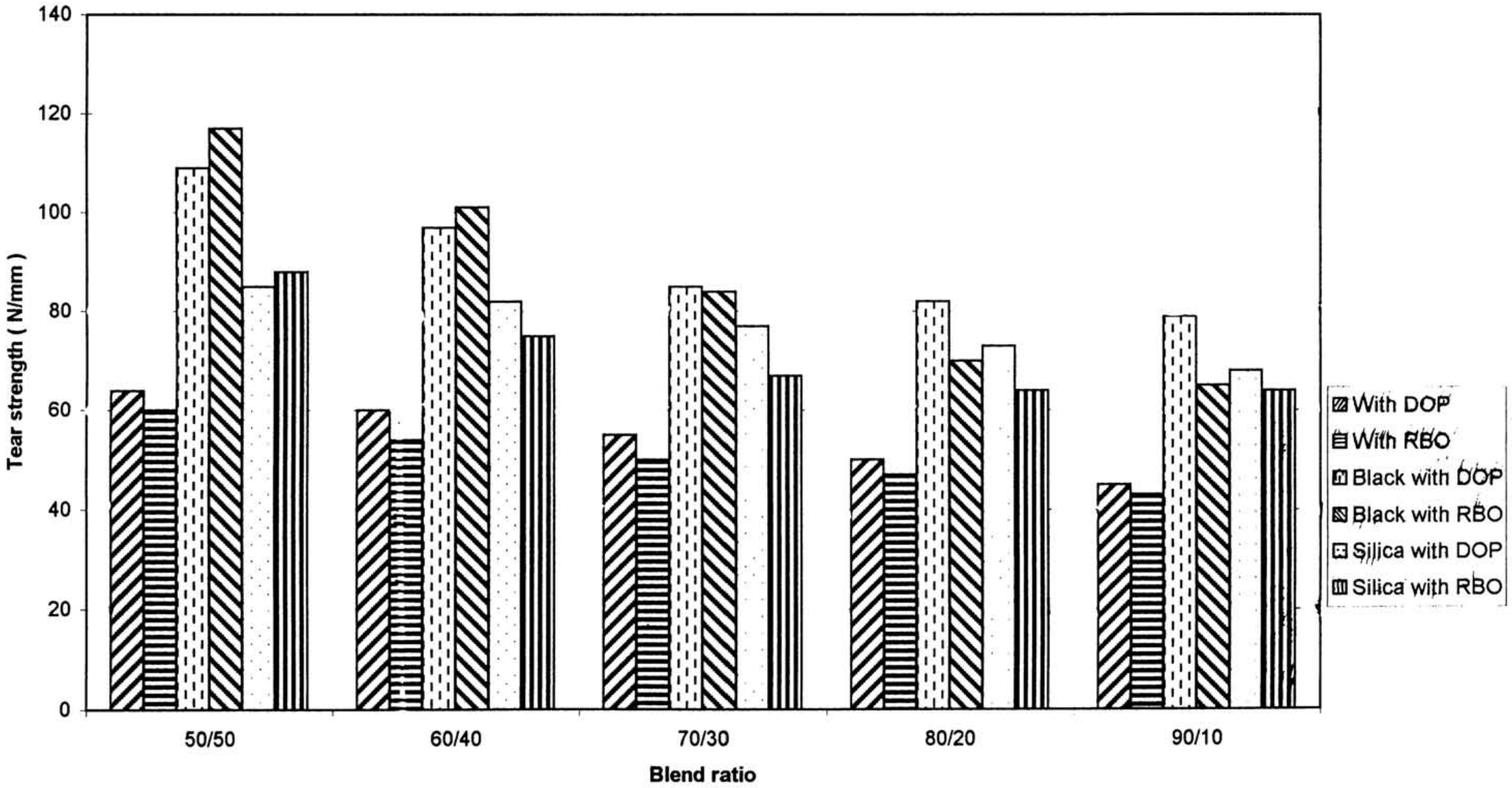


Fig 5.15 Variation of tear strength with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/RBO

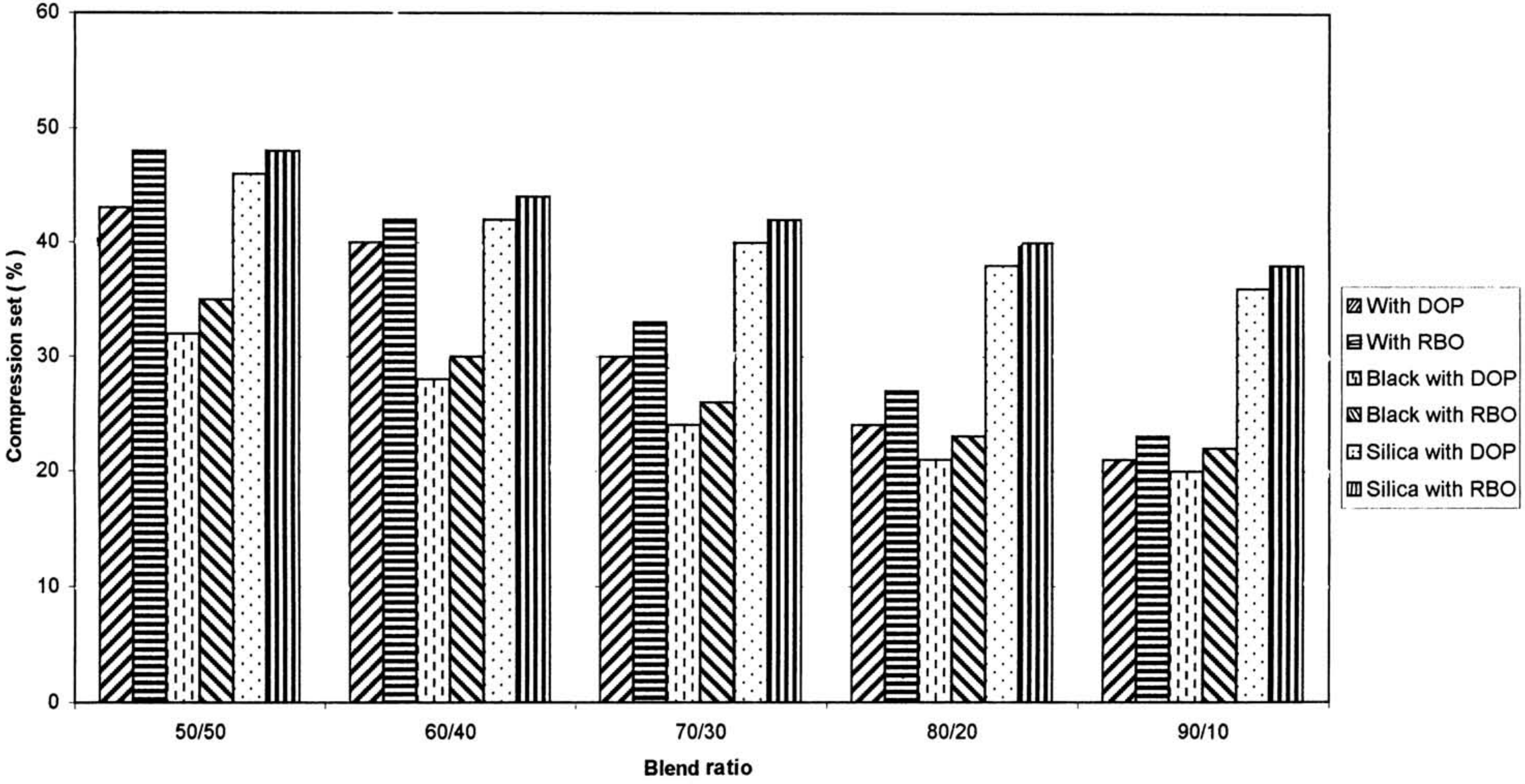


Fig 5.16 Variation of compression set with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/RBO

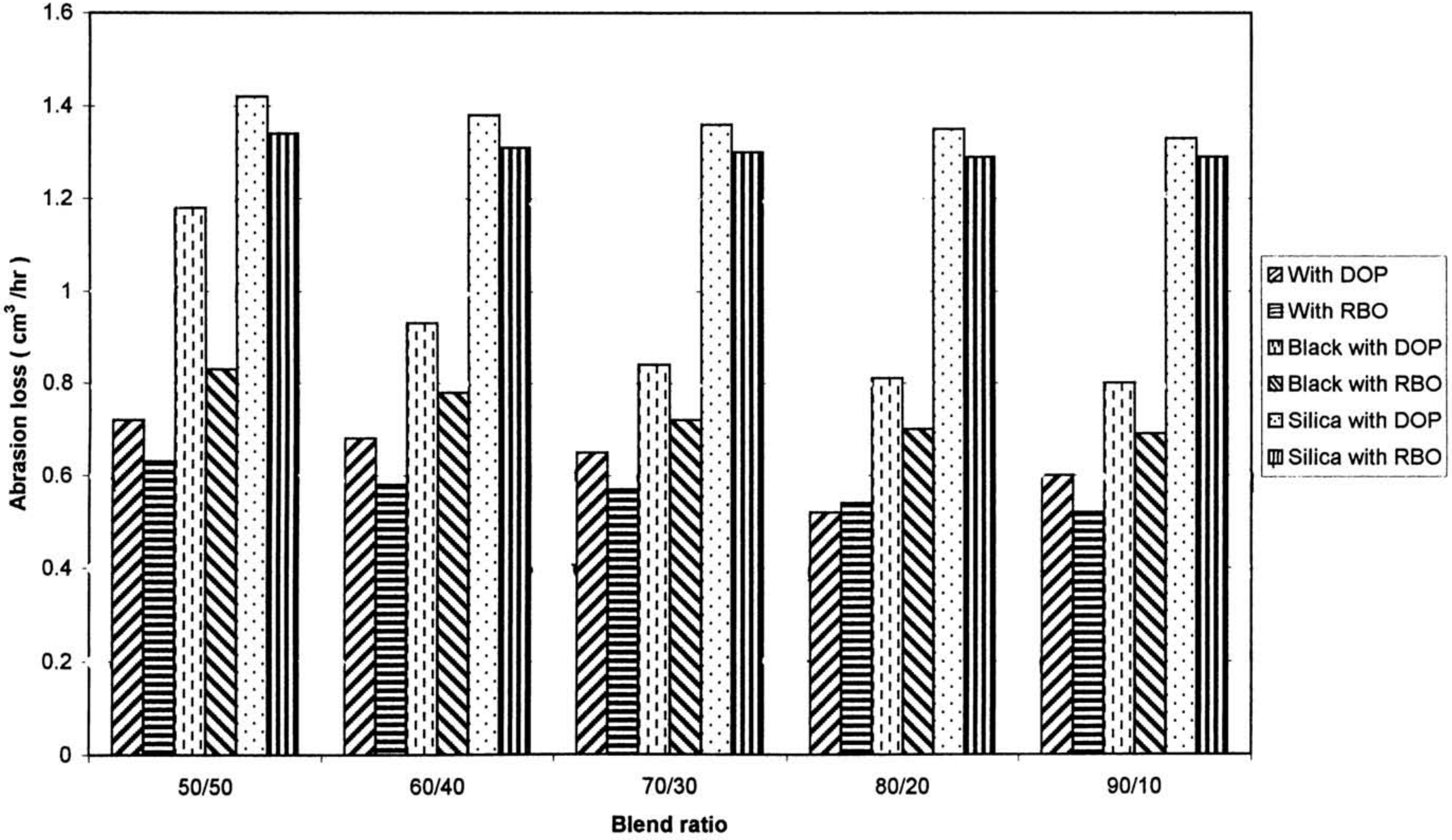


Fig 5.17 Variation of abrasion loss with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/RBO

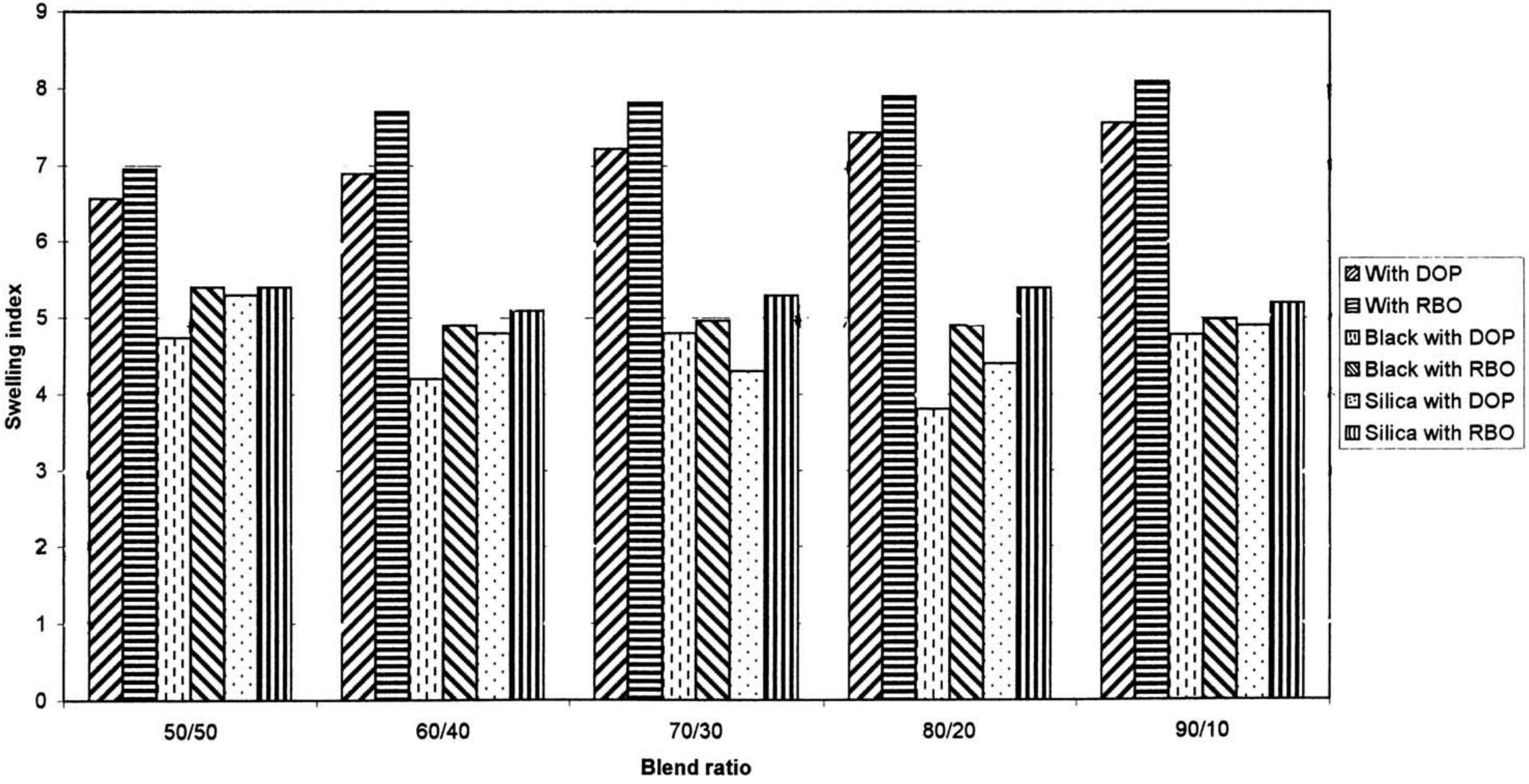


Fig 5.18 Variation of swelling index with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/RBO

Chapter VI

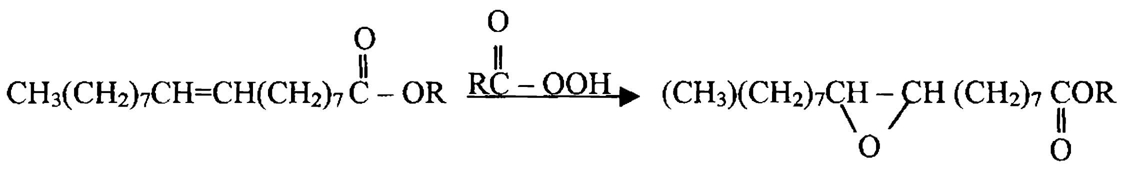
STUDIES ON THE USE OF EPOXIDISED RICE BRAN OIL AS PLASTICISER /STABILISER FOR NBR-PVC BLENDS

Plasticisers and stabilisers constitute the two major class of additives used in PVC compounding. Heat stabilisers constitute an unavoidable compounding ingredient in any PVC formulation. They prevent thermal degradation (dehydrochlorination) of the polymer in processing and in service. PVC degradation results in loss of hydrogen and chlorine atoms from adjacent carbon atoms in the polymer chain with the formation of HCl. The resulting C=C– bond weakens the adjacent (C–Cl) bond leading to the loss of further HCl and the formation of a second double bond. As a result of the repetition of this kind of reaction sequence of conjugated double bonds are formed in the polymer chain. Heat stabilisers are a class of compounds which interrupt the above reaction sequence by addition to the polymer chain to prevent the propagation and in addition to this they bind the released HCl molecules also. Most stabiliser systems used in commercial PVC formulations contain two or more compounds which operate synergistically. In the decreasing order of volume of consumption the main groups of PVC stabilisers used in flexible PVC may be classified into lead compounds, mixed metal compounds, organotins and auxiliary stabilisers. Basic lead salts viz., basic lead carbonate, tribasic lead sulphate, dibasic lead phosphate, and dibasic lead phthalate are the important cost effective lead compounds used in PVC as heat stabilisers. The strong opacifying effect of lead stabilisers makes them unsuitable for use in transparent or translucent products. Lead stearates have a dual function and act as lubricants as well as stabilisers. The mixed metal soap solids, partially soluble in plasticisers, can have plasticisation and compatibility effects. They are soaps of certain metals like calcium, zinc, barium etc. used in specific combination for synergistic effects. Most common organotin stabilisers are mixtures of mono and di-organotin compounds. Organotin stabilisers are characterised by high efficiency (but high cost) and outstanding clarity in PVC compounds. Auxiliary stabilisers are additives which are of limited benefit when used alone but which have a co-stabilising function when used in conjunction with primary stabilisers, particularly mixed metal type. The important members of this class of compounds are phosphates and epoxides. Phosphites $[P(OR)_3]$ are believed to function by chelating reaction products from the primary stabilisation mechanism, which would otherwise participate in degradation reactions.

E.H. Sorg et al[1] postulated that incorporation of plasticiser into PVC inhibited degradation during processing and offsets darkening and stiffening of the plastic. Several physical factors like increased lubricity decreased hot melt viscosity and separation of the PVC polymer chains from each other contribute to this phenomenon.[2] It is also noticed that the activation energy of dehydrohalogenation of polyvinyl chloride resin was unchanged when most plasticisers were added and the improved heat stability was due to the dilution by plasticisers. Plasticisers are used at times to make processing of the resin or fabrication of the final article easier without seriously changing the properties of the original resin. Thus proper choice of a plasticiser can aid processing by better internal lubricity, reduced stickening of the molten resin to the metal equipment, lower hot melt viscosity or improved resin stability. Butadiene-acrylonitrile rubbers (NBR) were used early as plasticisers in PVC. At higher concentration of PVC (50 to 85%) the blends with NBR become plasticised PVC, while at still higher concentration (>85%) the blends constitute one class of impact resistant PVC. It is also reported that NBR used early as plasticisers in PVC and now used in more complex polyblends usually lower the heat stability. However if they are used in very small amounts, they will act as heat stabilisers.[3] Frequently rubbery polymeric materials are added to the resin to give just enough elongation or enough softening to the PVC resin, at least in highly dispersed microregions, that it will withstand more mechanical stress. These impact modifiers are occasionally classified as plasticisers.

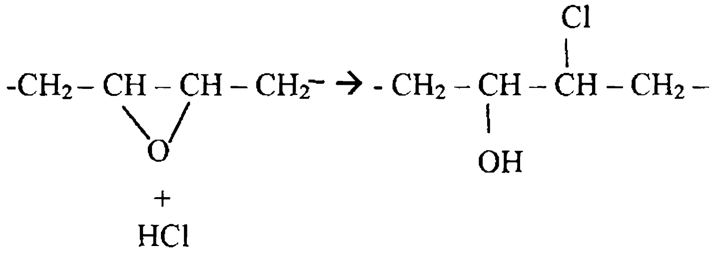
In PVC the main epoxy stabilisers are equally effective plasticisers also. They are either epoxidised natural product triglycerides (epoxy soya oil) or esters derived from triglycerides (eg. Octyl epoxy stearate). These two groups are normally described as epoxy oils and epoxy esters respectively. These compounds have a dual function in PVC acting both as co-stabilisers (usually in conjunction with mixed metal systems), and as plasticisers. In its use in PVC compounding the emphasis is usually given on its stabilising function, their plasticising activity being secondary or even incidental. Heat stabilising efficiency is related to oxirane oxygen content and this parameter is usually included in sales specifications. The modification of structure brought about by epoxidation also improves the PVC compatibility and permanence of the esters to an extent sufficient for them to be used as plasticisers. The compatibility limits of the epoxy plasticisers classify them as secondary plasticisers. Typical level of incorporation is around 6 phr at which they make a significant contribution to plasticisation and differences in performance between the different types become apparent. In practice safe levels of incorporation are much lower than might be determined in simple tests. The level of consumption of epoxy additives places them high in the non phthalate plasticisers.

Epoxidation may be defined as the formation of a three membered ether (oxirane) by the reaction of peracids with olefinic or aromatic double bonds. Oxiranes may also be formed by an internal SN_2 reaction of a chlorohydrin. The three membered ethers formed are also designated as 1-2 epoxides.



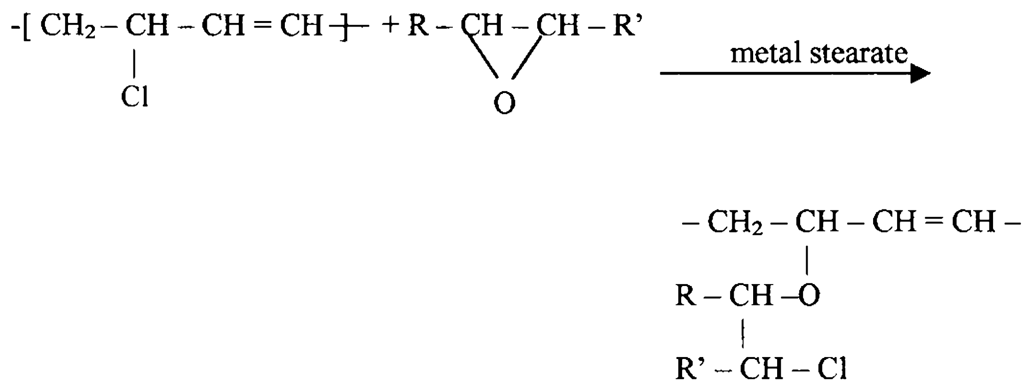
$$CH_3(CH_2)_7CH=CH(CH_2)_7\overset{\overset{O}{\|}}{C}-OR \xrightarrow{R\overset{\overset{O}{\|}}{C}-OOH} (CH_3)(CH_2)_7\underset{O}{\underbrace{CH-CH}}(CH_2)_7\underset{\underset{O}{\|}}{C}OR$$

The predominant heat stabilizing reaction of the epoxy additive is binding of hydrogen chloride by opening of the oxirane ring and thus retard the catalytic effect of HCl on degradation.[4]



$$-CH_2-\underset{O}{\underbrace{CH-CH}}-CH_2- + HCl \rightarrow -CH_2-\underset{OH}{\underset{|}{CH}}-\overset{Cl}{\overset{|}{CH}}-CH_2-$$

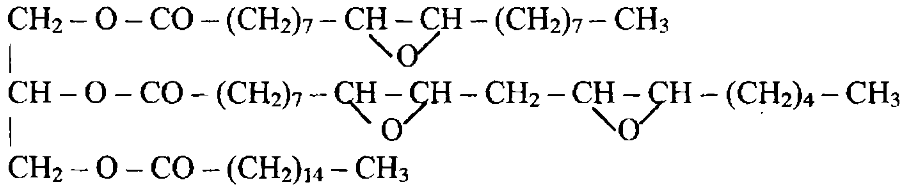
The epichlorohydrins thus produced in this reaction have low PVC compatibility and can cause surface exudation under some conditions to give a sticky surface deposit. A further undesirable potential reaction is polymerization involving the epoxy groups to give an incompatible non-plasticising polymer.[5] The vegetable oils used as raw materials for epoxidation are esters of glycerol with mixed C_{18} acids having a high level of unsaturation. The main such feed stocks are soyabean oil and linseed oil. The epoxidised products have molecular weight around 1000 which is well above those of phthalates and falls into the range of the lower molecular weight polyester plasticisers. They share with polyesters the characteristics of high viscosity, low plasticising efficiency and high resistance to migration. Epoxy soya bean oil is used in PVC food packaging films where its low contribution to migration helps to achieve conformance to the prescribed maximum limit for total migration of all additives.[6] The ability of epoxidised soyabean oil and other fatty acid oils to function as secondary stabilizers to improve the high temperature stability of PVC compounds is now well established. The cost and other physical property considerations restrict their use to 5 to 7 phr levels in PVC formulations. It is also noted that in addition to their role as HCl scavenger in PVC formulation, they can function as chain stopper for dehydrochlorination according to the mechanism given below:



Due to the pronounced catalytic effect of zinc and cadmium, epoxidised stabilizers find much usage with these mixed metal stabilizers.[7]

The epoxidised oils and epoxidised esters of unsaturated fatty acids are widely used in PVC and its co-polymers in conjunction with other substances to impart a spectrum of properties like heat and light stability, superior ageing and low temperature flexibility. Epoxidised products also find their use in the formulation of anti-corrosive coatings, adhesion and alkyl resin castings.[8] Attempts have also been made to make use of non-edible oils, instead of ground nut oil which is at present employed for epoxidation in India.[9] Khuddus et al.[8] have reported the epoxidation of cotton seed, safflower and tobacco seed oils. Nagiah and others[10] have studied the epoxidation of linseed oil, castor oil and sardine oil. Jain and Bhatnagar worked out the conditions for the preparation of epoxidised acetylated castor oil.[9] Han et al[11] have reported the preparation of epoxidised silk worm pupae oil having an oxirane content of 6.4% and its use as a plasticiser in PVC. Muthiah et al[12] investigated the epoxidation of watermelon seed, sesame, miger seed, rice bran and ajowan seed oils. Thermal stability of PVC blends is very much subjected to interaction effect from liquid plasticisers like phthalates, epoxides etc. used in the formulation. In fact epoxy plasticisers are added to PVC formulation as a part of PVC thermal stabilization.[13] The use of linseed oil as such as a plasticiser in PVC is reported.[14] Epoxidised linseed oil is widely used in plastics and rubbers as plasticiser and heat stabilizer.[15]

In view of the fact that the use of epoxidised vegetable oils in PVC compounds imparts good heat stability, low temperature flexibility and better ageing resistance to the PVC formulation when used together with conventional heat stabilizers, we thought it worthwhile to use epoxidised rice bran oil as a plasticiser in the preparation of NBR-PVC blends. This chapter reports the results of this study using ERBO (structure as given below) with an epoxy content of 3.4%. The blends are prepared in different blend ratios using carbon black/silica as fillers. In order to ascertain the behaviour of the blends in the absence of fillers, gum NBR-PVC blends were also prepared in different blend ratios. All the blends so prepared were evaluated for their cure characteristics and the vulcanisates were tested for the different tensile properties.



A typical constituent of epoxidised rice bran oil

EXPERIMENTAL

For the present study NBR and PVC having the specifications as detailed in chapter II were used. Zinc oxide, magnesium oxide, stearic acid, mercapto benzothiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, carbon black (HAF 330), silica, dioctyl phthalate used are all of commercial grade. For the preparation of epoxidised rice bran oil, epoxidation of the crude oil using hydrogen peroxide (30%), and acetic acid in presence of H_2SO_4 as catalyst was employed. In the above reaction H_2O_2 and organic acid react in presence of the mineral acid to form the peracid, which in turn react with the oil to effect the epoxidation. An inert solvent like benzene is used to reduce the effect of H_2SO_4 in catalysing epoxy ring opening. The epoxy content of the oil was determined. The detailed experimental procedure and the procedure for the determination of oxirane content is given in chapter II. ERBO having an epoxy content of 3.4% was used for the present investigation. A stabiliser system consisting of ZnO, MgO and stearic acid was used for the PVC resin.

The PVC resin was first mixed with stabilisers and the formulation of the mix is as shown in Table 6.1 where DOP is the control. This PVC compound was then thoroughly mixed with plasticiser (DOP/ERBO) so as to get absorbed into the PVC resin. NBR-PVC blends were prepared in a Brabender plasticorder model PL3S. The mixing head of the plasticorder was heated to 150°C and the rotor speed was adjusted to 50 rpm. The mill masticated NBR was first added to mixing chamber and allowed to heat up and homogenise for one minute. PVC compound was then added over a period of five minutes and mixing was continued for two more minutes till a constant torque was obtained in the torque rheometer. The final compounding of the NBR-PVC blends prepared in different blend ratios (50/50, 60/40, 70/30, 80/20, 90/10) using fillers and DOP/ERBO was done in a laboratory model two-roll mill at a temperature of 80°C as per the formulation given in Tables 6.2, 6.3 and 6.4. The amount of curatives used in the blend was selected on the basis of weight percentage of NBR in the blend. For the preparation of silica filled blends 1.5 phr diethylene glycol was used in order to offset the cure retardation property of the

Table 6.1 Formulation of the PVC Compound

Ingredients	Phr
PVC	100
ZnO	4
MgO	4
Stearic acid	2
DOP/ERBO	20

Table 6.2 Formulation of the NBR compound in the unfilled blend

Ingredients	Phr
NBR	100
Sulphur	1.5
ZnO	3
Stearic acid	1
Styrenated phenol	2
MBTS	1.5
TMTD	0.5

Table 6.3 Formulation of NBR (black filled)

Ingredients	Phr
NBR	100
Sulphur	1.5
ZnO	3
Stearic acid	1
Styrenated phenol	2
MBTS	1.5
TMTD	0.5
Carbon black (HAF 330)	40
DOP/ERBO	4

Table 6.4 Formulation of NBR (silica filled).

Ingredients	Phr
NBR	100
Sulphur	1.5
ZnO	3
Stearic acid	1
Styrenated phenol	2
Precipitated silica	60
Diethylene glycol	1.5
MBTS	1.5
TMTD	0.5
DOP/ERBO	6

silica, thereby preventing the acidic silica adversely affecting the cure reactions. When carbon black was used as the filler 4 phr of DOP/ERBO was used as processing aid and for silica filled blends 6 phr DOP/ERBO was used. This quantity was derived based on our earlier studies on processability of NBR as detailed in chapter III. The final compound so prepared was kept for maturation at 27°C for a period of 24 hr.

The processability study of the NBR-PVC blend using DOP/ERBO was carried out in a Brabender plasticorder. The temperature of the test chamber of the plasticorder was set at 150°C and the initial rotor speed was adjusted to 50 rpm. For each blend ratio the total weight of all the blend ingredients were so selected as to keep the total weight at 40 gm. The nitrile rubber was first masticated by passing six times in a two roll mill at a nip gap of 0.8 mm to get a thin sheet. This was then cut into small strips before feeding into the plasticorder. The total mixing time was kept at 8 minutes with the following break up. The rubber was first allowed to heat up and allowed to homogenise for one minute, then PVC resin premixed with ZnO, MgO, stearic acid, DOP/ERBO was added over a period of 5 minutes, the mixing was allowed to continue for two more minutes. The final torque (in Mgms) reading in the torque rheometer was recorded. The experiment was repeated with different blend ratios (50/50, 70/30) using different levels of DOP/ERBO (15, 20, 25 phr) at different rpms (50, 70 and 90). Viscosity (torque/rpm) of the different blends under review is plotted against corresponding rpm for different levels of oil used so as to get the flow curves.

The cure characteristics of the compounds were determined at 160°C on a Geottfert elastograph model 67.85. The important cure parameters reported are mentioned below. Time taken for attaining 90% of the maximum torque is reported as the optimum cure time. Time taken for 10% vulcanisation is taken as the Elastographic scorch time. The cure rate index is calculated using the formula $100/t_{90}-t_{10}$, where t_{90} and t_{10} are the times corresponding to the optimum cure and ten percent vulcanisation respectively. The maximum – mininum torque ($MH_F - ML$) of each mix under study is also reported. The compounds were vulcanised upto their optimum cure time in an electrically heated laboratory type hydraulic press at 160°C at a pressure of 11.764 MPa. The tensile properties of the vulcanisate were determined on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min. as per ASTM designation D 412-87 Method A. Dumbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Heat ageing was carried out at 100°C for 96 hr in an air oven. Tear resistance is tested as per ASTM designation D 624-86 using angular test pieces. Compression set was tested as per ASTM D 395-86 method B. Abrasion resistance was evaluated using DIN abrader (DIN 53516). The swelling index of the different samples were determined by immersing 0.2 gm of the sample in chloroform for 24 hr. All these experiments are described in detail in chapter II.

RESULTS AND DISCUSSION

Processability characteristics

The optimisation of the required minimum amount of DOP/ERBO needed for the preparation of the blend was done in a Brabender plasticorder by varying the amounts of these plasticisers during the blend preparation. For the experimental blends like 50/50 and 70/30 NBR-PVC; 15, 20, 25 phr levels of DOP/ERBO were tried during blend preparation at 150°C. From the flow curves shown in Fig.6.1 and 6.2 it is evident that an acceptable torque values (below 30 Nm) was obtained when 15, 20, 25 phr each of DOP/ERBO were used irrespective of the blend ratio at 150°C and 50 rpm. But a near absence of white patches (due to unfused PVC particles) on the surface of the thin sheet of blends prepared by passing through a two roll mill at a nip gap of 0.8 mm was noted when 20 phr levels of DOP/ERBO was used for the blend preparation. Hence 20 phr levels of DOP/ERBO may be taken as the optimum level. The lower viscosity values (Figs.6.1 and 6.2) of the blends prepared with ERBO over the ones prepared with equal loading of DOP may be attributed to the better plasticising nature of ERBO compared to DOP.

From the flow curves (Figs.6.1 and 6.2) it is also evident that the blend under review is pseudoplastic as seen from the decrease in viscosity values with increase in rpm. It is also noticed that when the amount of ERBO increased beyond 25 phr the preparation of the blend was found to be cumbersome, as the torque developed was too small to get a uniformly mixed blend within the stipulated period. The experimental blends prepared using 20 phr ERBO (based on the percentage weight of PVC in the blend) were compared with DOP with regard to cure characteristics and different physical properties. The results of these investigations are discussed in the subsequent section. The processability study indicates that DOP could safely be replaced with ERBO and that the latter offers less torque during the preparation of the blend in the Brabender plasticorder compared to DOP. On economic and technological considerations also this aspect will

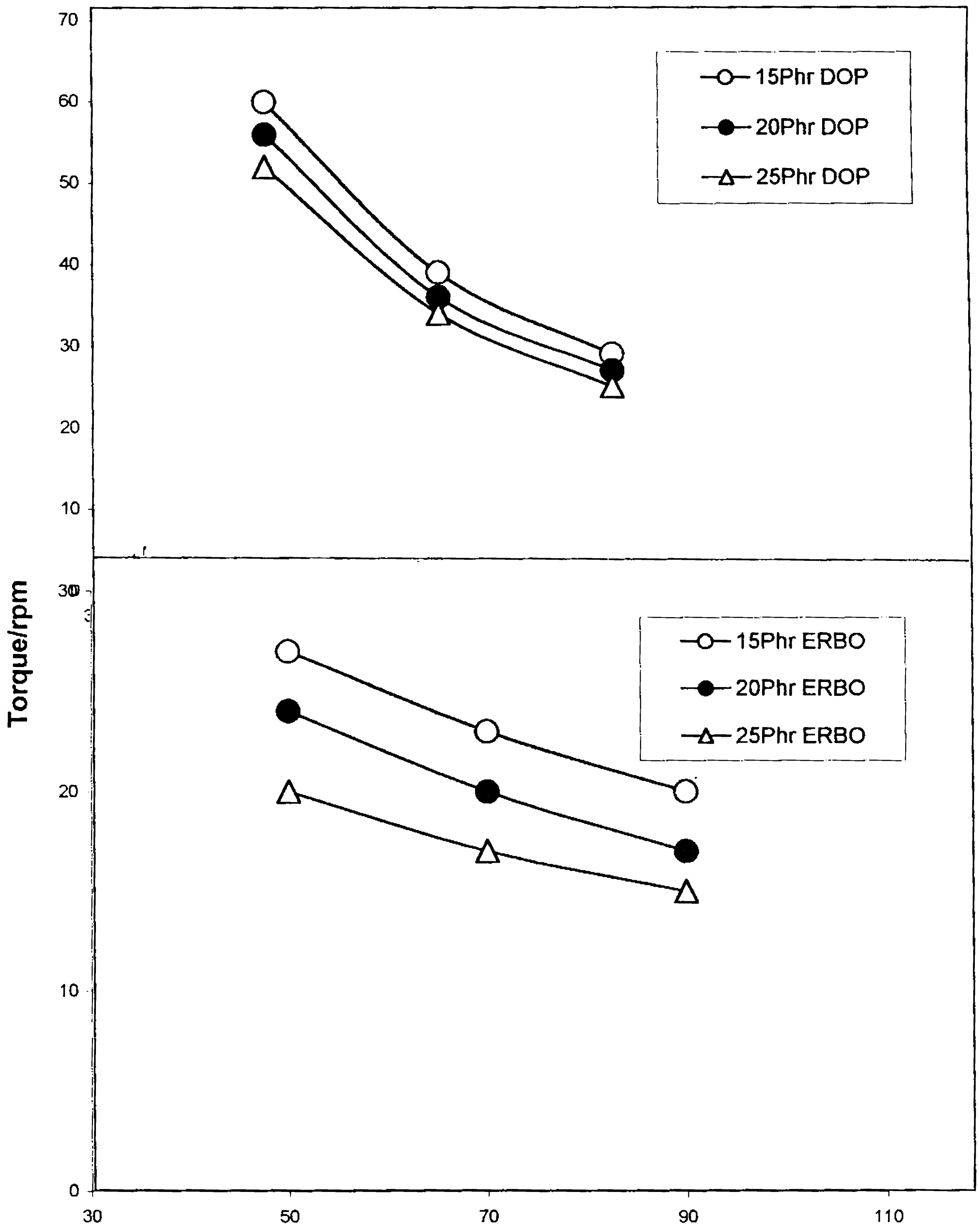


Fig. 6.1 Flow curves of 50/50 NBR-PVC blend prepared with different levels of DOP/ERBO at 150°C

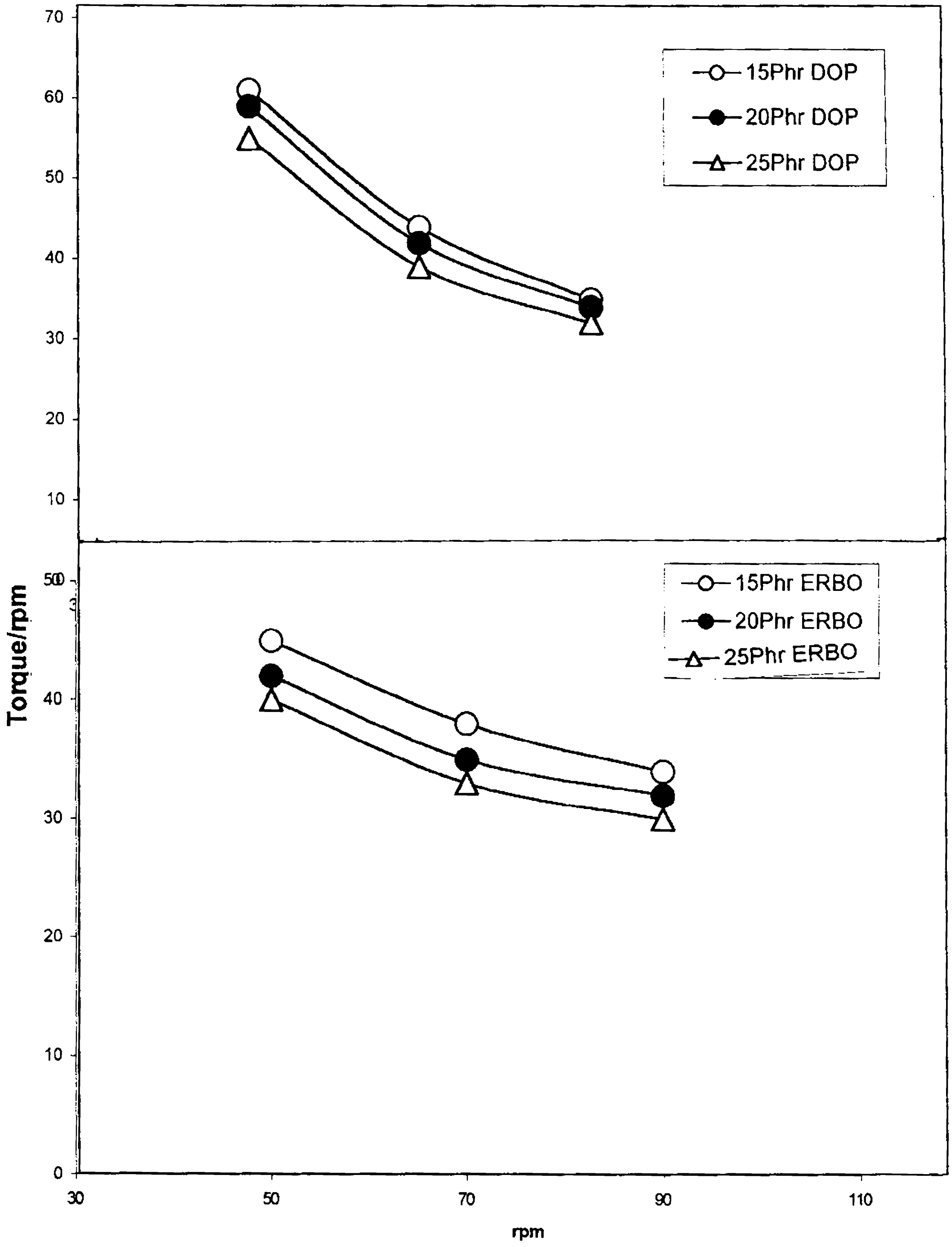


Fig. 6.2 Flow curves of 70/30 NBR-PVC blend prepared with different levels of DOP/ERBO at 150°C

have beneficial effect as the heat development during the preparation of ERBO based blends will be lesser. Moreover the price of ERBO will be less compared to the other epoxidised oils currently being used in PVC industry, as the raw unedible rice bran oil is available at a very low price in India. In addition to this aspect the ERBO may be used for the preparation of NBR-PVC as this oil is devoid of any toxic effect compared to DOP.

Cure characteristics

The cure characteristics of the different blends prepared with ERBO/DOP were evaluated using Goettfert elastograph at 160°C. The cure curves of these blends are given in Fig.6.3 and that of the black and silica filled blends are given in Figs.6.4 and 6.5 respectively. The corresponding cure characteristics are given in Tables 6.5–6.7. From the figures it is evident that the blends prepared with ERBO give lower torque values compared to the corresponding control blends prepared with DOP. The better compatibility and lesser plasticising nature of DOP over ERBO towards the blend constituents may be attributed to this observation. This trend is shown by other blends prepared with fillers like carbon black and silica also (Figs. 6.4 and 6.5). From the cure time values of different blends it is evident that ERBO based blends give lower optimum cure time values and hence higher cure rate compared to the control mixes. This effect is more pronounced for the black filled blends. However the scorch time values (time before the onset of vulcanisation) is slightly higher for silica filled blends prepared with DOP compared to the ones prepared with ERBO. But the unfilled and black filled blends prepared with DOP/ERBO showed almost similar scorch time values. Thus it may be concluded that the DOP based silica filled blends will have slightly better processing safety

Table 6.5 Cure characteristics of NBR-PVC blends with DOP/EBRO

	50/50		60/40		70/30		80/20		90/10	
	DOP	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**
Maximum torque MH_F (Nm)	0.121	0.078	0.198	0.095	0.208	0.141	0.224	0.171	0.236	0.194
Minimum torque ML (Nm)	0.013	0.02	0.018	0.02	0.016	0.02	0.014	0.02	0.014	0.02
(MH_F-ML) (Nm)	0.108	0.058	0.180	0.075	0.192	0.121	0.210	0.151	0.222	0.174
Optimum cure time t_{90} (min)	7.6	7.5	7.4	7.0	5.8	5.2	5.2	4.8	3.9	3.0
Elastographic scorch time t_{10} (min)	2.0	2.0	1.8	2.0	1.9	1.9	1.8	1.9	1.8	1.9
Cure rate index	18	18	18	20	26	30	30	35	48	91

Table 6.6 Cure characteristics of black filled NBR-PVC blends with DOP/EBRO

	50/50		60/40		70/30		80/20		90/10	
	DOP	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**
Maximum torque MH_F (Nm)	0.139	0.116	0.207	0.164	0.218	0.206	0.280	0.270	0.301	0.295
Minimum torque ML (Nm)	0.069	0.05	0.06	0.05	0.06	0.05	0.06	0.05	0.05	0.05
(MH_F-ML) (Nm)	0.070	0.066	0.147	0.114	0.158	0.156	0.22	0.22	0.251	0.245
Optimum cure time t_{90} (min)	12.50	5.4	6.2	4.8	5.5	4.6	4.9	3.8	2.7	2.6
Elastographic scorch time t_{10} (min)	1.9	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.5	1.7
Cure rate index	9.4	27.02	22.0	32.2	26.0	34.5	31.0	47.6	83.0	111.0

Table 6.7 Cure characteristics of silica filled NBR-PVC blends with DOP/EBRO

	50/50		60/40		70/30		80/20		90/10	
	DOP	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**	**DOP**	**ERBO**
Maximum torque MH_F (Nm)	0.267	0.214	0.279	0.254	0.434	0.40	1.01	0.90	1.08	0.96
Minimum torque ML (Nm)	0.174	0.126	0.185	0.180	0.20	0.18	0.20	0.20	0.22	0.20
(MH_F-ML) (Nm)	0.093	0.088	0.094	0.074	0.234	0.22	0.81	0.70	0.86	0.76
Optimum cure time t_{90} (min)	12.2	6.0	6.6	5.4	5.4	3.8	3.6	3.2	2.8	2.6
Elastographic scorch time t_{10} (min)	2.3	1.7	1.9	1.7	1.3	1.1	1.1	1.0	1.0	0.90
Cure rate index	10.1	23.2	21.2	27.0	24.4	37.0	40.0	45.5	55.6	58.8

compared to the ERBO blends. But the lower optimum cure time and the corresponding higher cure rate of the ERBO blends will be of definite advantage.

Crosslink density

The swelling index of the different blends prepared with DOP/ERBO were determined using chloroform as the solvent and these values of the different blends are shown in Fig.6.6. From the graph it is evident that DOP based blends show lower swelling index values and hence higher crosslink density compared to the ERBO blends. Slightly better compatibility of DOP over ERBO towards the blends components might be cited as the reason for this observation. The higher $MH_F - ML$ (Maximum – Minimum torque values) of DOP based blends, both with and without fillers is further supported by the above observation as there exist a direct relationship between crosslink density and maximum-minimum torque values. It may therefore be concluded that for better crosslink density of the NBR-PVC blends, incorporation of DOP is preferred to ERBO.

Tensile properties

The tensile strength values of the different blend vulcanisates prepared with DOP/ERBO without and with fillers viz. carbon black and silica are given in Fig.6.7. From the figure it may be noted that tensile values are slightly higher for vulcanisates prepared with DOP irrespective of the blend ratio or the nature of the filler used for the preparation of the blend. This trend is in accordance with the corresponding crosslink density values reported above. The elongation at break values are slightly higher for the blends prepared with DOP as shown in Fig.6.8. After ageing the different blend vulcanisates prepared with DOP/ERBO at 100°C for 96 hr, it is found that for unfilled and silica filled blends the percentage retention of tensile values are more for the ERBO based blends (Fig.6.9). For the black filled blends the percentage retention of tensile values are more or less same for both DOP and ERBO based blends. However the percentage retention of elongation at break values are slightly higher for the blends prepared with ERBO compared to the control blends prepared with DOP and the same trend is seen in the filled systems also (Fig.6.10). This is especially so when the blends are richer in NBR phase. This may be attributed to the additional role played by ERBO as a heat stabiliser in addition to plasticiser, by virtue of the presence of epoxy groups in the oil. A comparison of 200% modulus values is shown in Fig.6.11 and as expected the values are slightly higher for blends prepared with DOP. This observation is seen reflected in the corresponding crosslink density values and tensile properties of the DOP based blends.

Other physical properties such as tear strength, abrasion resistance and compression set of the different blend vulcanisates are also evaluated. The results of these are given in Figs.6.12, 6.13 and 6.14 respectively. From the graph it is evident that the tear strength values are slightly lower for the blends prepared with ERBO over the corresponding control blends prepared with DOP. It is again noted that the tear values are progressively decreasing as the percentage of the PVC in the blend decreases, irrespective of the nature of the filler in the blend. It is a clear indication of better tear strength afforded by PVC in presence of a more compatible plasticiser like DOP to the different blends under review. The abrasion loss values of the different blend vulcanisates are given in Fig.6.13 and these are found to be slightly higher for the unfilled and black filled blends prepared with ERBO over the DOP based control blends. But, for the silica filled system the reverse trend is observed especially when the blend is richer in NBR phase. The higher abrasion loss values of ERBO based unfilled and black filled blends may be attributed to the lesser degree of interaction between the blend components in presence of ERBO compared to the control mixes prepared with DOP. The compression set values are also seen to be slightly higher for the ERBO based blends both with and without fillers. However the set values are decreasing as the percentage weight of NBR in the blend increases. This may be attributed to the greater rubber chain flexibility of the blend due to the lesser amount of PVC.

CONCLUSIONS

1. From the processability studies it may be concluded that the incorporation of equal loading of ERBO instead of DOP in the blend recipe has both economic and technological advantage. The maximum torque developed is less when ERBO is used as a plasticiser. Thus both power and time may be saved during the blend preparation.

2. A comparison of cure characteristics NBR-PVC blends based on ERBO/DOP show that ERBO exhibits cure accelerating property. The higher cure rate values of ERBO based blends will have advantage during the vulcanization step.

3. A comparison of the physical properties of the DOP/ERBO based blends show that the replacement of DOP by ERBO has slight adverse effect on these properties.

But the higher retention of percentage elongation after ageing of the ERBO based blends may be considered as an advantage.

4. Cost-wise also use of ERBO will be advantageous as the raw material for the preparation of the epoxidised rice bran oil is available very cheap in India. Further, as stated earlier, ERBO can be recommended as a nontoxic plasticiser/stabiliser substitute for the blend preparations under review.

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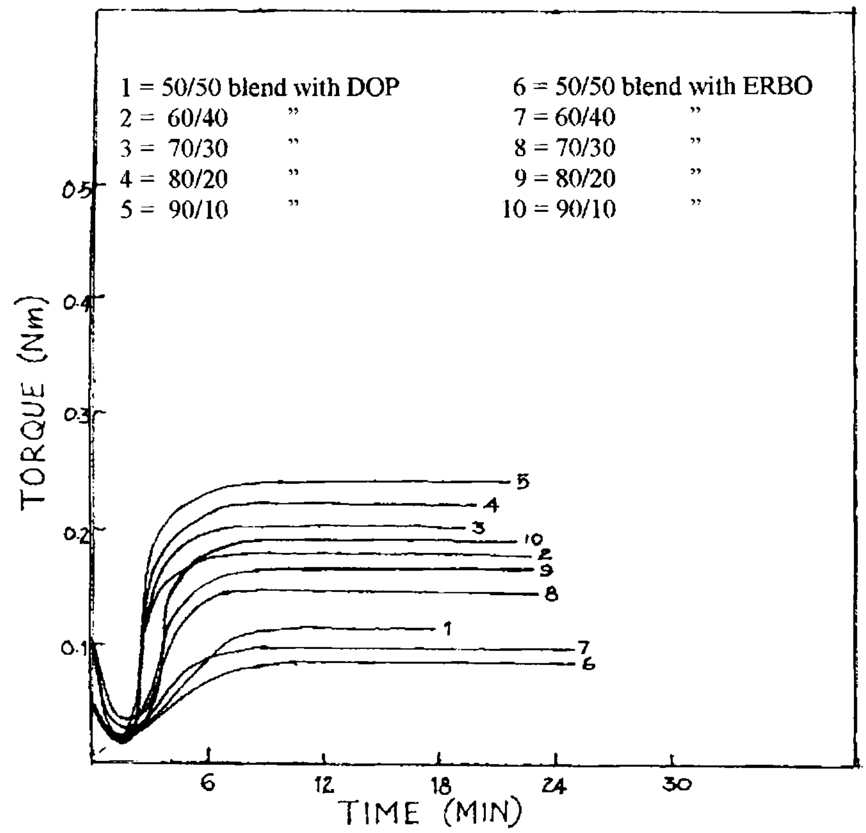

Fig. 6.3 Cure curves of NBR-PVC blends with DOP/ERBO

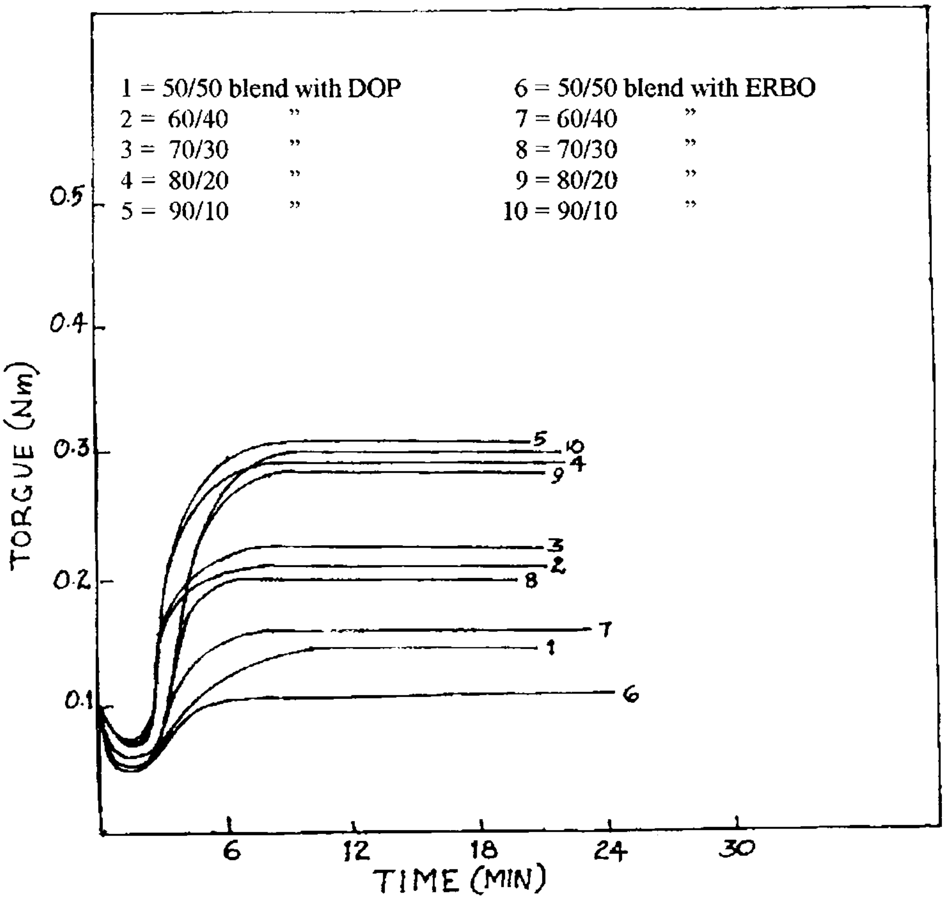

Fig. 6.4 Cure curves of black filled NBR-PVC blends prepared with DOP/ERBO

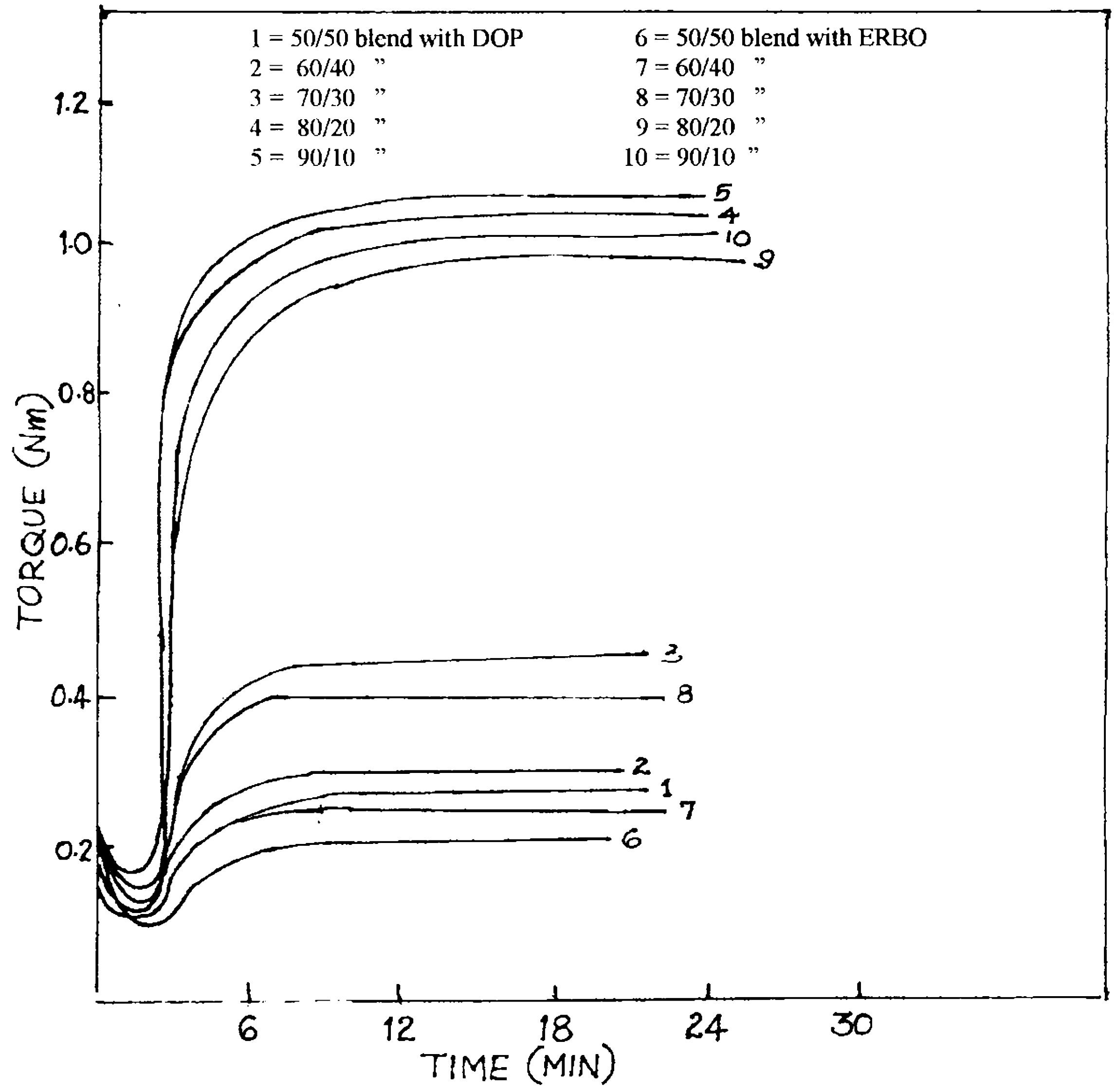

Fig. 6.5 Cure curves of silica filled NBR-PVC with DOP/ERBO

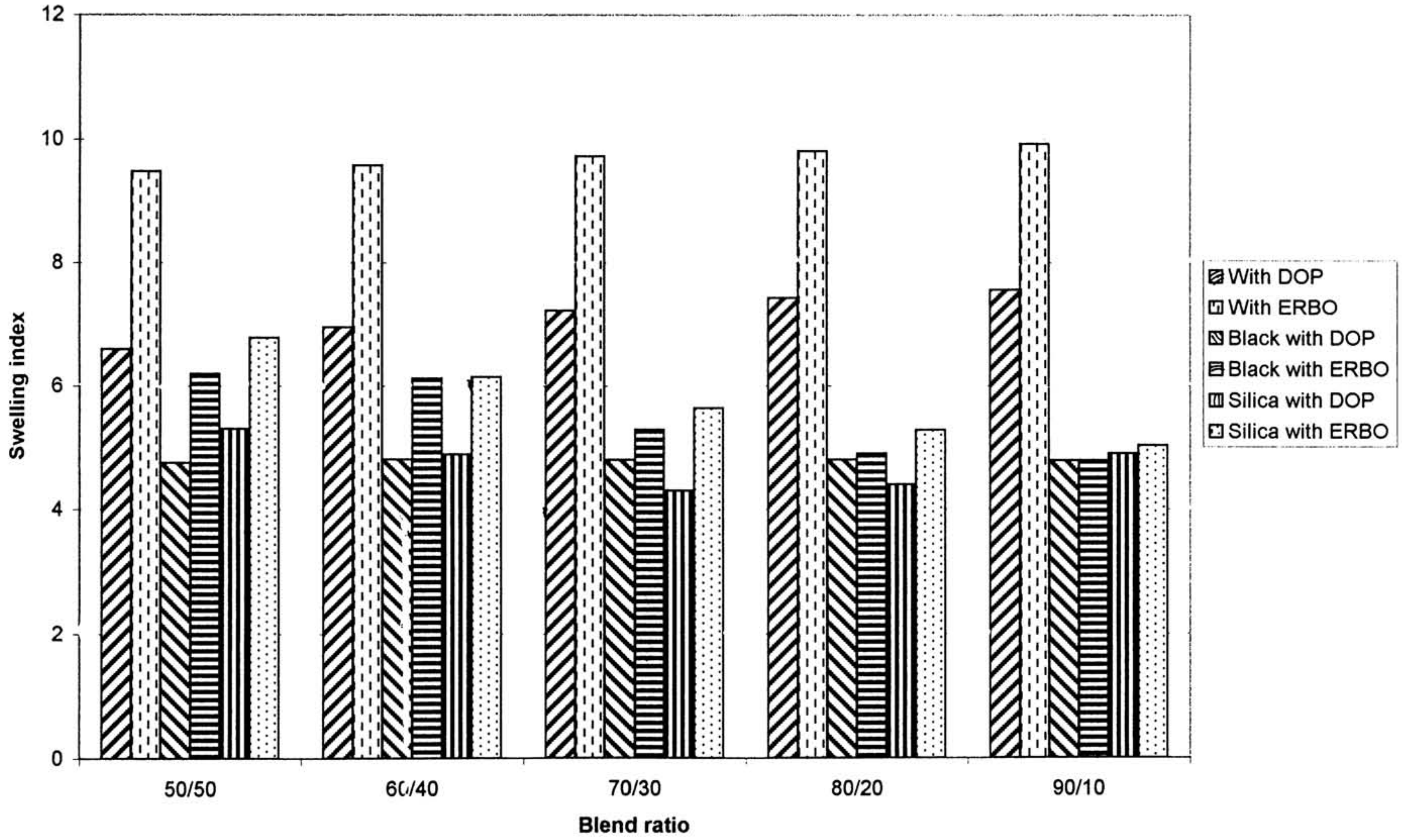

Fig 6.6 Variation of swelling index with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

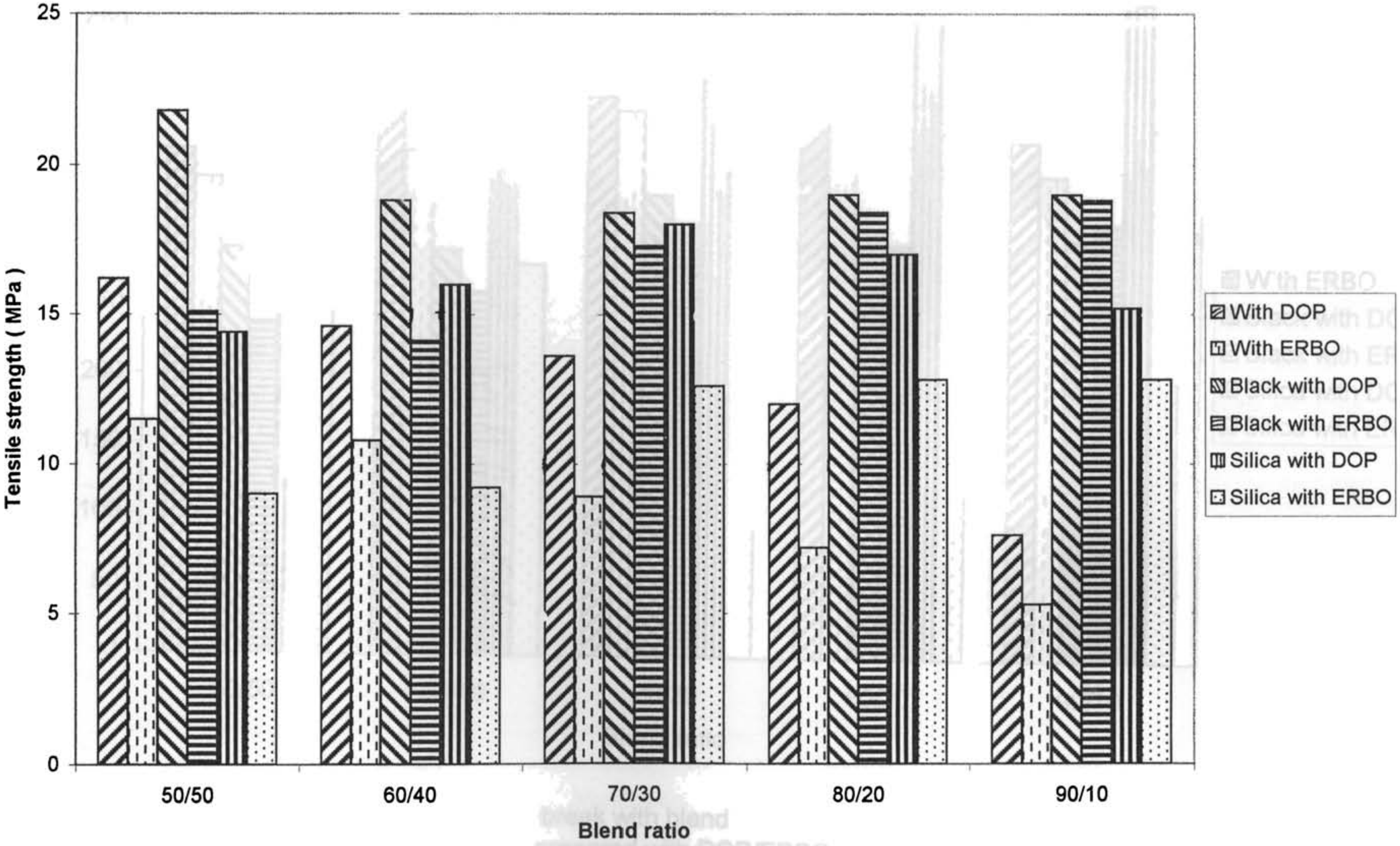

Fig. 6.7 Variation of tensile strength with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

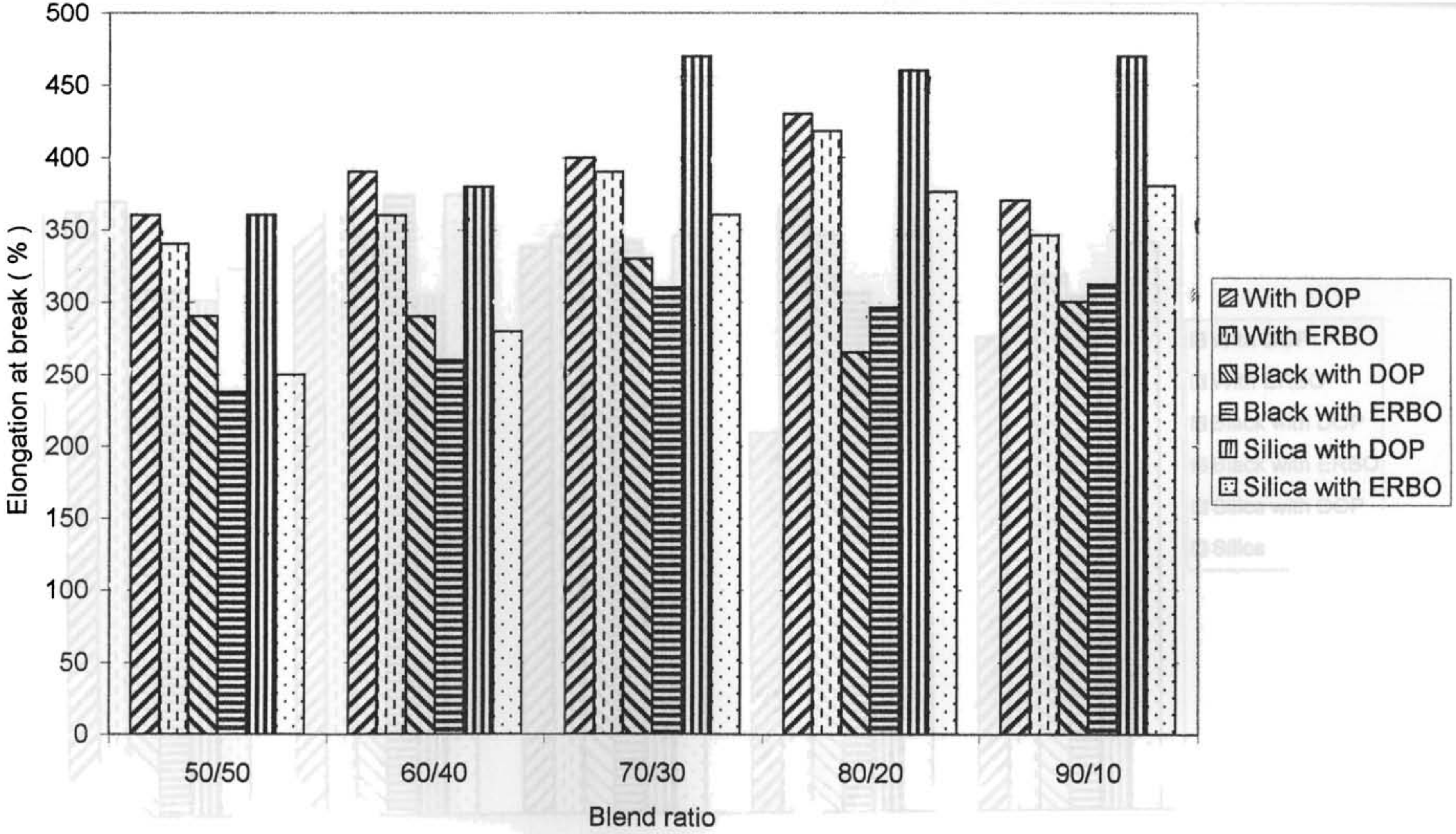

Fig. 6.8 Variation of % elongation at break with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

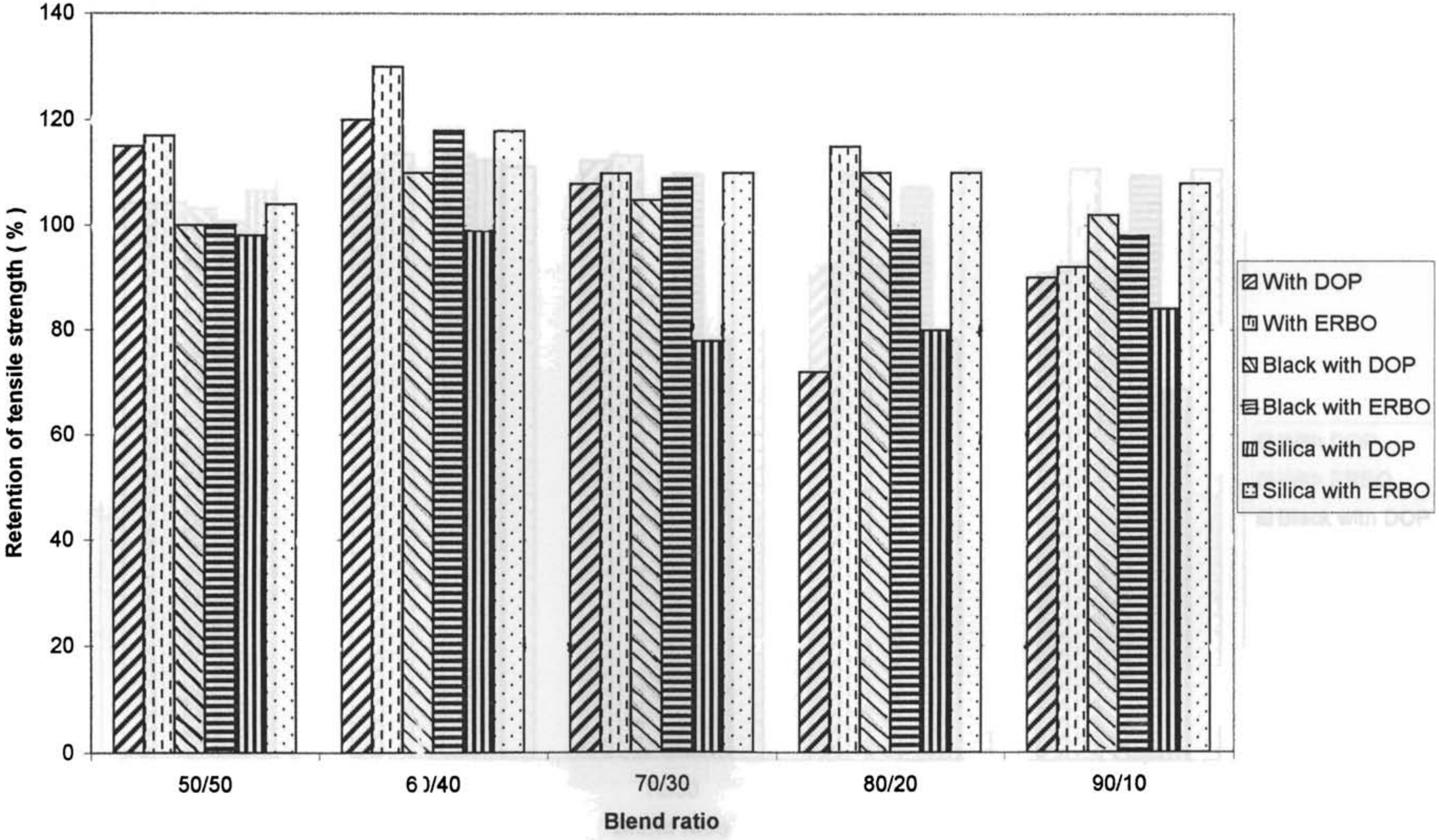

Fig. 6.9 Variation of % retention of tensile strength with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

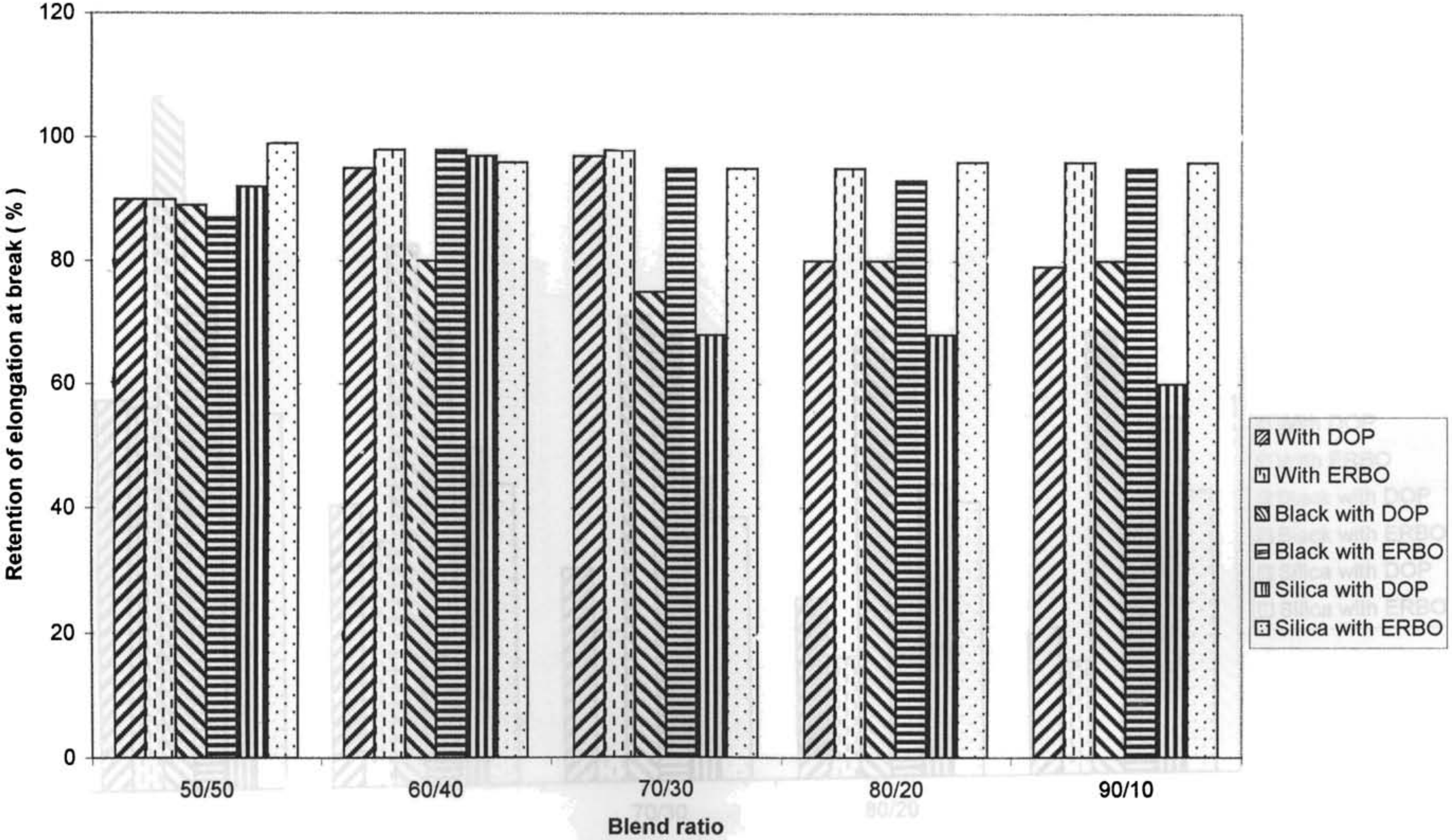

Fig 6.10 Variation of % retention of elongation at break with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

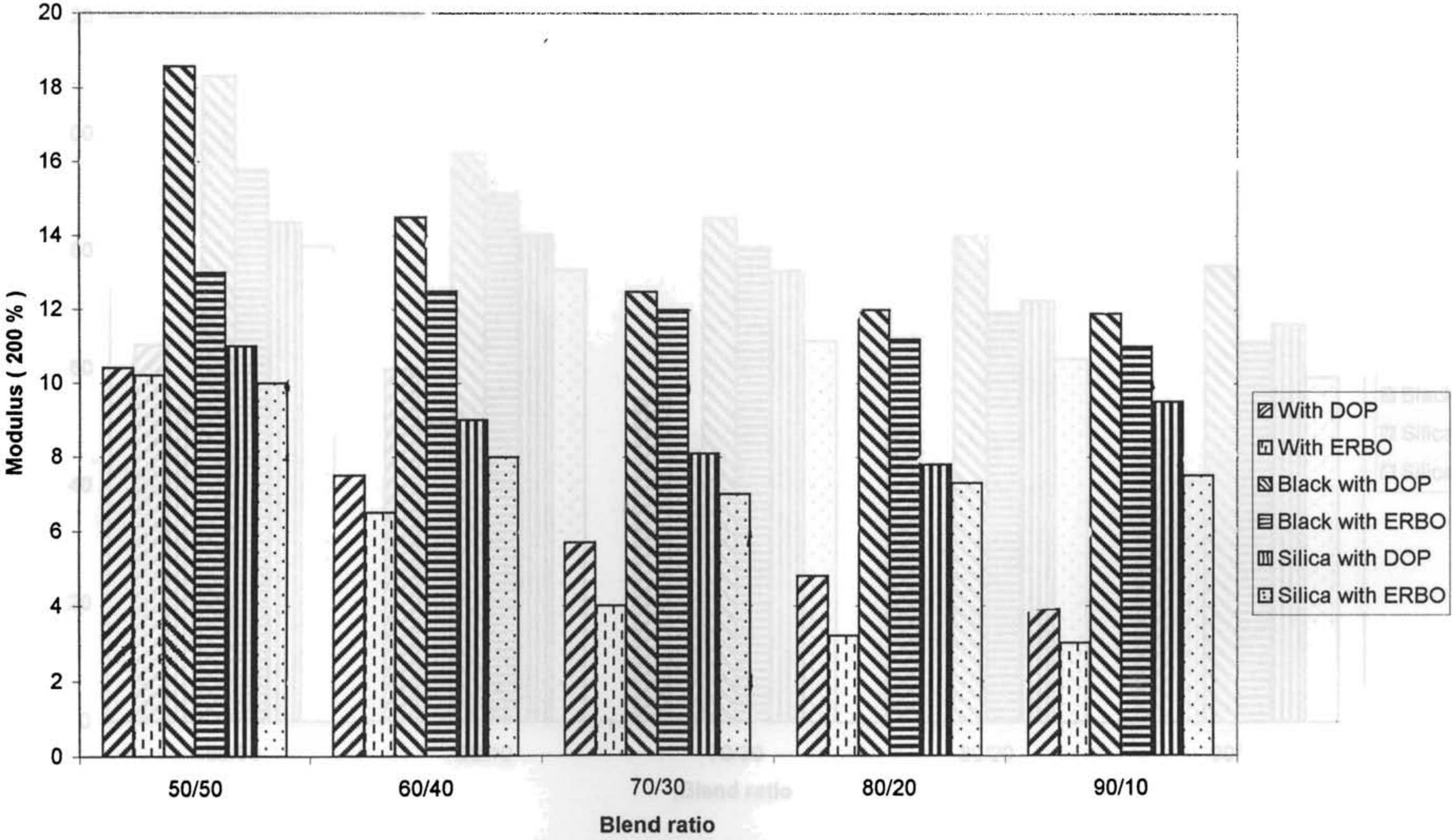

Fig 6.11 Variation of 200 % modulus with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

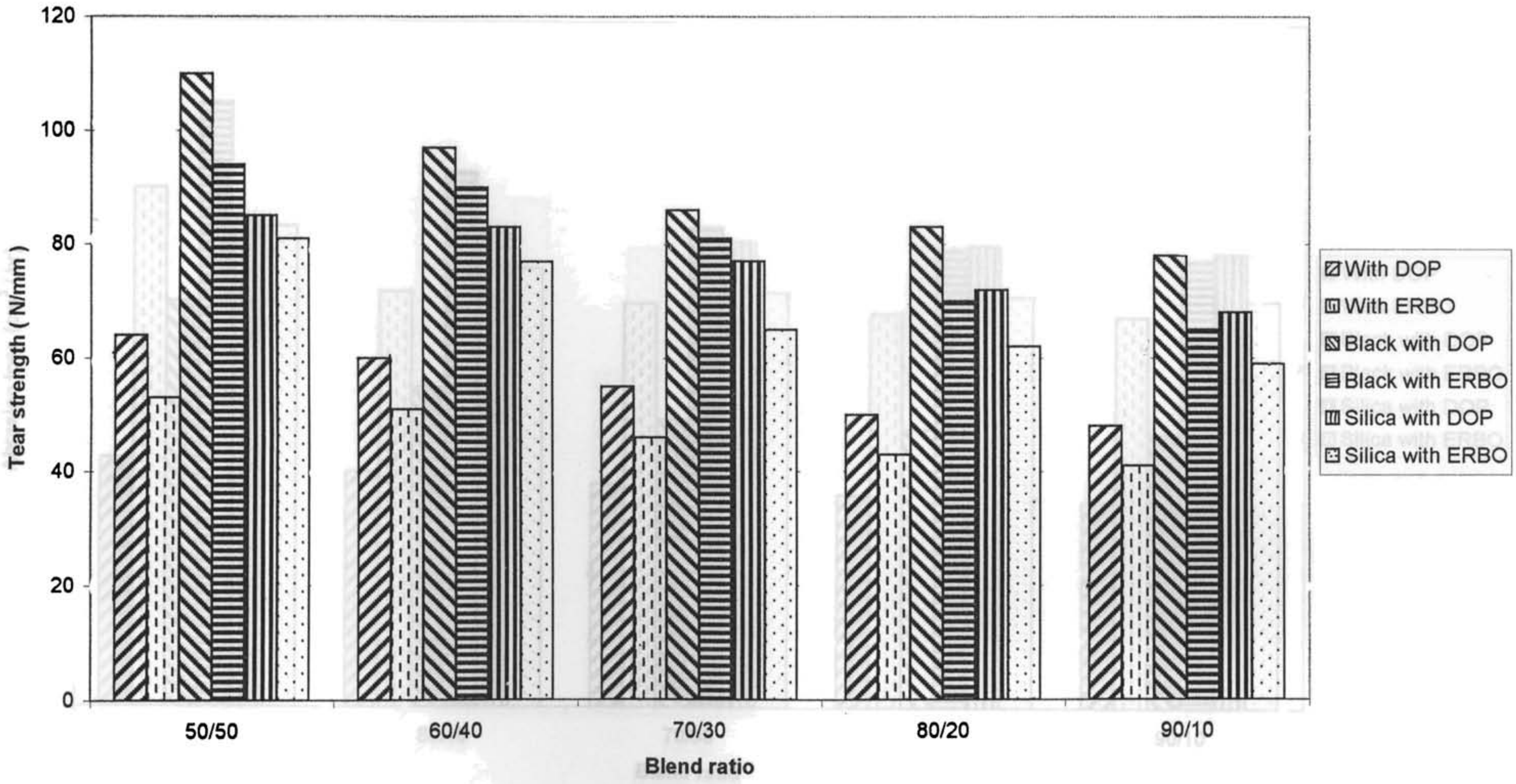

Fig 6.12 Variation of tear strength with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

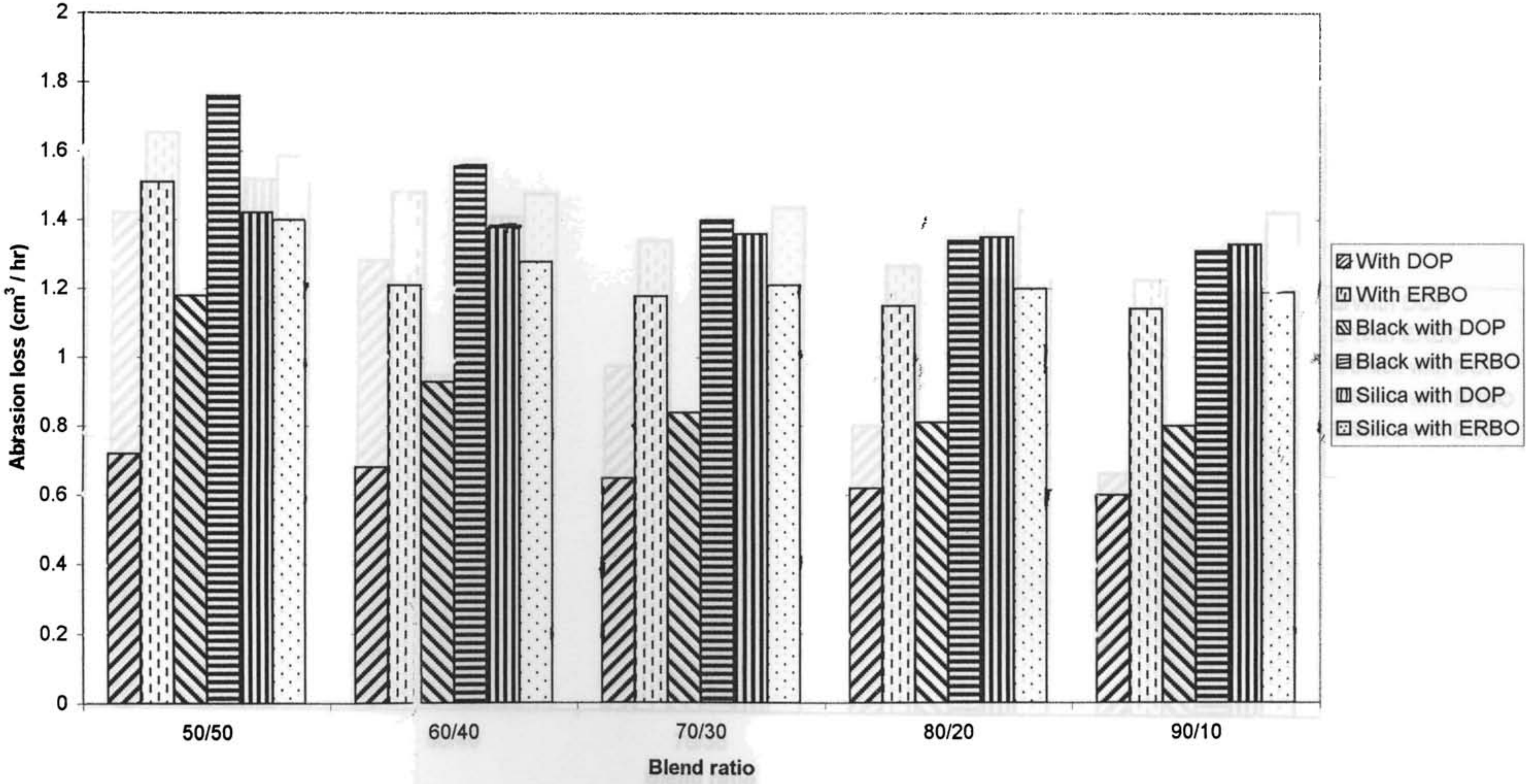

Fig. 6.13 Variation of abrasion loss with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

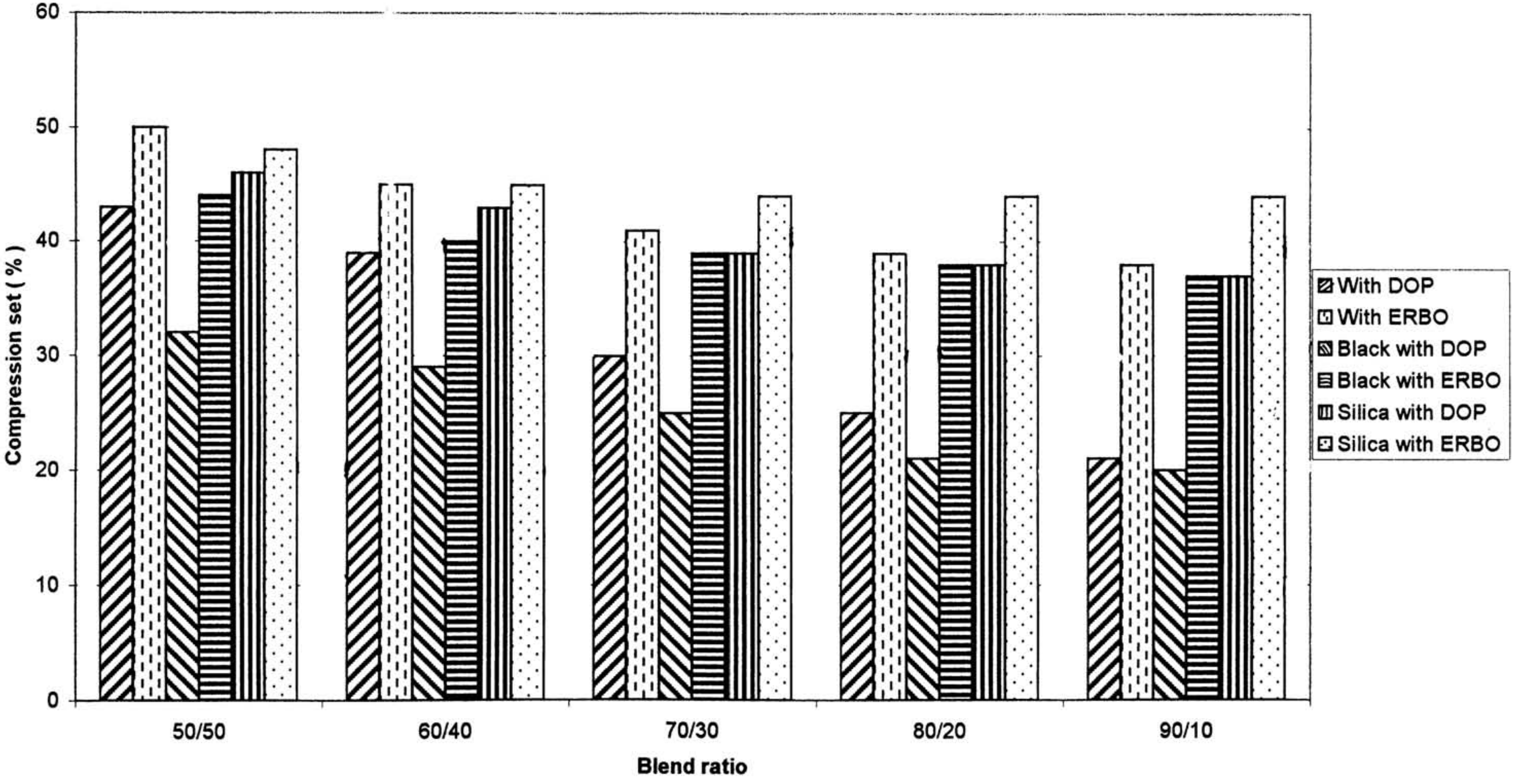

Fig 6.14 Variation of compression set with blend ratio of black/silica/unfilled NBR-PVC blends prepared with DOP/ERBO

CHAPTER VII

Chapter VII

SUMMARY AND CONCLUSIONS.

The main part of the present work deals with the utilization of a cost effective and ecofriendly natural product viz. rice bran oil(RBO) and its derivative(epoxidised rice bran oil-ERBO) as substitutes for the conventional processing aids in the compounding of two polar rubbers and their different blends. Compounding and evaluation of various physical properties of polychloroprene(CR) and acrylonitrile butadiene(NBR) rubbers and their blends with natural rubber(NR) and polyvinyl chloride (PVC) have been investigated. RBO and ERBO were tried along with other compounding ingredients in the above mentioned systems and their processing characteristics and the properties of the respective vulcanisates obtained were compared with those of the control mixes prepared with conventional process aids.

India is the second largest rice producing country in the world and produces large quantities of raw rice bran oil. Though the country is producing large amounts of this oil, its use as an edible oil is limited because of its high free fatty acid (FFA) content. In order to produce edible grade oil the bran should be stabilized and the enzyme lipase present in the bran should be deactivated. This enzyme present in the bran catalyses the hydrolysis of lipids into fatty acids. Since the rice milling process is not in the organized sector, it is impossible to have uniformly stabilized bran for the production of edible grade oil in India. The high FFA oil now being produced in the country finds its application mainly in soap industry as a substitute for other vegetable oils. One of the notable features of rice bran oil is its exceptional shelf life over other vegetable oils. This feature is attributed to the presence of natural antioxidants like tocopherol and oryzanol which inhibit the occurrence of rancidity in the oil. The cholesterol lowering property of the oil is also attributed to the presence of natural antioxidants. Chemical composition of the oil shows that besides natural antioxidants it contains significant amount of free fatty acids. It may be noted that more than 80% of free fatty acid present in the oil constitute unsaturated fatty acids of which monosaturated acids constitute 40-45%.

In the conventional compounding of rubbers, besides other ingredients, processing aids, co-activators (higher fatty acids) and antioxidants are essentially included. The present study aims at the utilisation of rice bran oil as processing aid during compounding, co-activator during vulcanisation stage and as an antioxidant to minimise the aging effect during service life. This aim of the study is based on the fact that rice bran oil can function as a process aid, the higher fatty acids in it will be useful as a co-activator and the antioxidants present can have antiageing properties.

The thesis is divided into seven chapters. In the first chapter a general discussion on processing aids, their mechanism of action in the rubber compounds, their physical and chemical characteristics etc have been included. Literature survey on the use of various kinds of vegetable oils and their chemically modified forms in the rubber compounding is also included in this section. A detailed description of rice bran oil with special emphasis on its extraction from rice bran, its chemical composition, stability and antioxidant property etc are discussed in detail. The present uses of RBO in various fields have also been included. A brief description on rubber compounding with special emphasis on the role of activators and accelerators in the vulcanisation reaction has been incorporated. Polymer blends and their important classifications are also discussed in general in this chapter.

In the second chapter the specifications of different polymers and the important compounding ingredients used in the study are included. A general description of the different experimental procedures adopted is also included in this section. Processability study and details of blend preparations have also been included in this part of the thesis. Preparation of epoxidised rice bran oil having the required epoxy content is also detailed here. Chemical test methods like determination of free fatty acid content of RBO, determination of iodine value, estimation of the epoxy content of ERBO etc are included. A brief description on the importance of physical tests on vulcanisates of rubber compounds and various ASTM methods for the determination of physical properties like tensile strength, tear strength, compression set, abrasion resistance etc have also been detailed in this section. Determination of the chemical crosslink density of the different vulcanisates is also explained in this chapter.

In chapter three the results of the investigations on the use of rice bran oil as multipurpose compounding ingredient in two polar rubbers viz. nitrile and polychloroprene are included. Apart from the use as a process aid the oil was tried as a co-activator in place of stearic acid for these rubbers. The antioxidant styrenated phenol also was replaced from the compounding recipe of these two rubbers by virtue of the presence of antioxidants in the oil. The epoxidised variety of the oil (ERBO) was also tried as a processing aid for these two rubbers. The processing behaviour of RBO and ERBO were compared with that of onventional processing aids used in thse rubbers viz. DOP and aromatic oil. The quantity of the oil required is optimised by using different quantities and processing them in a Brabender plasticorder. The processability study showed that the maximum torque developed was more or less same when DOP/ aromatic oil was replaced with RBO /ERBO from the different compound recipes. The mixes prepared using RBO and ERBO and those containing conventional process aids are evaluated for the different cure characteristics like development of torque, scorch time, optimum cure time, cure rate index etc. The results of these investigations showed that the cure properties of the experimental mixes were not adversely affected when DOP/ aromatic oil was replaced with RBO or ERBO in the different mixes under review. The replacement of stearic acid and antioxidant from the RBO based mixes of these rubbers showed that neither the cure characteristics nor the vulcanisate properties had been adversely affected. Rice bran oil based mixes showed lower optimum cure time values which indicate the cure accelerating nature of the oil . A comparison of the cure curves of the RBO and ERBO based mixes with the respective controls showed that former mixes gave lower torque values which is an indication of the better plasticising nature of these oils giving processing advantage. Again from the cure curves it is evident that none of the compounds show any tendency for reversion on cure.

The initial tensile strength values are slightly higher for the vulcanisates prepared with DOP/aromatic oil compared to the ones prepared with RBO/ERBO. This is seen reflected in the corresponding cross link density values of the above mixes. The aging resistance of the RBO and ERBO based mixes of NBR and CR are better compared to the control mixes prepared with DOP/aromatic oil. This is indicative of the antioxidant nature of the oils. Other physical properties like compression set, hardness, tear strength etc of RBO and ERBO based mixes of these two rubbers are comparable to the respective control mixes. Abrasion loss values of NBR and CR vulcanisates containing

RBO and ERBO are lower compared to the control mixes showing better abrasion resistance of the rice bran oil based mixes. This may be attributed to the better interaction of filler with rubber in presence of RBO /ERBO.

From the results obtained from this study it may be concluded that raw rice bran oil, having high free fatty acid content (and which is non edible) may be utilised as a multipurpose compounding ingredient in special purpose rubbers like nitrile and polychloroprene. It may be noted here that conventional process aids like naphthenic and aromatic oils are petroleum based and are found to contain benzene and polycyclic aromatic hydrocarbons(PAH) which are known carcinogens. Cost-wise also petroleum based processing aids are not economical as of now. Rice bran oil is a nontoxic, natural product available at cheaper rate in India and its use in the rubber compounding will be of definite advantage.

When it was found that RBO and ERBO could advantageously be used as process aids in polychloroprene rubber, it was thought worthwhile to use these oils in the compounding of a filled blend like NR-CR which is more or less incompatible in nature. Blends are broadly classified into compatible and incompatible depending on the solubility parameter of the component rubbers. Blends of rubbers having closest solubility parameter are classified as compatible whereas the ones with large difference in solubility parameter values are classified as incompatible. In chapter four the use of RBO and ERBO in place of aromatic oil for the compounding of carbon black filled NR-CR blend is discussed. The most important criterion to be considered while selecting a plasticiser for a given rubber is its compatibility. As a general rule polar plasticiser is preferred for polar rubbers and the non polar ones for the non polar rubbers. Natural oils are characterised by two opposing effects towards compatibility. A large portion of the molecule of the oil is made up of long paraffinic chains which are rather wax like in character and hence tend to give low compatibility towards polar polymers where as the ester groups present in the same molecule confer some degree of polarity and improve compatibility towards such polymers. The processing behaviour of RBO and ERBO in these mixes were compared with that of aromatic oil. The quantity of the oil required is optimised with the help of a Brabender plasticorder. The flow curves of the 70/30, 50/50 and 30/70 NR-CR blends based on 4 phr of RBO/ERBO/aromatic oil showed more or less similar torque values for aromatic oil and RBO containing blends. However the torque developed was lower for ERBO based blends compared to control blends prepared with aromatic oil.

The cure characteristics of the mixes from the above different formulations were evaluated and it was found that optimum cure time values were slightly lower for the blends prepared with RBO and ERBO compared to the ones prepared with aromatic oil indicating cure acceleration of the natural oil. The scorch time values are also found to be less for the RBO and ERBO based blends compared to the reference blends. From the cure curves of the different blends prepared as above it is evident that none of the blends showed any tendency for reversion in cure . The maximum torque developed was found to be more or less same when RBO/aromatic oil was used as processing aid. However when ERBO was used the torque development was found to be less compared to the control blends . The tensile strength values of the RBO/ERBO/aromatic oil based vulcanisate are comparable. The retention of the tensile values of the RBO and aromatic oil based blends are more or less similar whereas for ERBO based blends these values are more than those of the control blends. The percentage retention of elongation at break values is also higher for the blends prepared with ERBO. This is an indication of the higher antioxidant function of ERBO when present in the blend. The cure characteristics and mechanical properties of the 50/50 blend based on RBO suggest that this oil could be used even in the absence of stearic acid for the vulcanisation of the blend without compromising on these properties . The tear strength and compression set values are more or less same for the blends containing RBO/aromatic oil. Tear strength values of vulcanisates from blends containing ERBO are found to be higher compared to the reference blends. Abrasion resistance of the vulcanisates based on RBO/ERBO are found to be better compared to the control blends. All these results and processing characteristics reported earlier indicate that rice bran oil and epoxidised rice bran oil can advantageously be used as process aids in the compounding of a carbon black filled non compatible blend like those of polychloroprene and natural rubber.

In the fifth chapter the suitability of rice bran oil as a plasticiser for a compatible rubber-plastic blend like that of NBR and PVC in different blend ratio is investigated. The efficiency of rice bran oil as a plasticiser both in the presence and absence of fillers like carbon black and silica is evaluated. The properties of the different blend vulcanisates based on RBO were compared with those based on DOP. The processing characteristics of these blends were also evaluated using a plasticorder. Results of the processability study indicate that 20 phr of rice bran oil on the weight basis of PVC would be required for the preparation of the blend. Addition of the oil above this level gives torque values which are insufficient to give a uniform blend at the experiment temperature of 150°C. From these studies it was also evident that the torque developed was less when rice bran oil was used as a plasticiser in place of DOP. This shows better blending efficiency of this oil. Comparison of the cure characteristics of the different blends based on RBO/DOP showed that the mixes containing RBO gave lower optimum cure time values over the respective control blends. This observation points to the cure accelerating effect of rice bran oil in a rubber-plastic blend also. Consequently scorch time values are also found to be less for RBO based blends. This is more evident in the case of silica filled systems. The maximum torque developed for all the DOP based blends (with and without fillers) is higher compared to the ones prepared with RBO . This may be explained to be due to the better plasticising nature of rice bran oil as indicated earlier. The lower torque values and cure accelerating effect of the RBO based blends over the ones with DOP will have technological advantage as both power and time can be saved during the different processing operations. A comparison of the mechanical properties of the blends prepared with DOP and RBO shows that DOP based blends have slight advantage in mechanical properties. However the abrasion resistance was found to be better for the RBO based vulcanisates. After ageing the different vulcanisates at 100°C for 96 hr, it is found that the percentage retention of tensile strength values are higher for silica filled blends prepared with RBO compared to the ones with DOP. However, a reverse trend is noted for unfilled and black filled blends.

Chapter six deals with use of epoxidised rice bran oil as a plasticiser/stabiliser for NBR -PVC blends prepared in different blend ratio. Epoxidised oils and epoxidised esters of unsaturated fatty acids are widely used in PVC and its co-polymers in conjunctions with other substances to impart heat stability and better aging properties . The epoxy oils and esters have dual functions in PVC, acting both as co-stabilisers and as plasticisers. It may be noted that the ERBO can prevent the degradation of the PVC resin by acting as a scavenger for HCl molecules by opening of the oxirane ring and thus retard the catalytic effect of HCl on the degradation of the resin. In this study epoxidised rice bran oil was tried as a plasticiser for the above blend preparation and its effects were evaluated both in the presence and absence of fillers like carbon black and silica . The processability study of the different blends using the plasticorder by varying the amount of epoxidised oil showed that 20 phr ERBO on the weight basis of PVC was sufficient for the blend preparation. A comparison of the cure characteristics of ERBO/DOP based blends showed that the mixes prepared with ERBO gave lower optimum cure time values and correspondingly higher cure rate. The scorch time values for the unfilled and black filled blends prepared with DOP/ERBO are found to be more or less similar. However the scorch time of silica filled ERBO blends are found to be less compared to the reference blends prepared with DOP. The torque developed for all the blends prepared with DOP are higher compared to the ones prepared with ERBO.

Comparison of the physical properties of DOP/ERBO based blends show that the DOP based vulcanisates have slightly better physical properties over the ERBO based ones. However the percentage retention of tensile strength values are higher for the unfilled and silica filled blends containing ERBO compared to the reference blends prepared. For the black filled blends the percentage retention of tensile values are more or less same for both DOP and ERBO based formulations. The percentage retention of elongation at break values are higher for all the blends prepared with ERBO. This is more evident when the blends are richer in NBR phase. This may be attributed to the heat stabilizing action of the epoxidised rice bran oil by virtue of the presence of oxirane rings in the oil.

LIST OF ABBREVIATIONS

AA	After ageing
ACN	Acrylonitrile
Ar.oil	Aromatic oil
ASTM	American Society for Testing and Materials
BA	Before ageing
BR	Polybutadiene
CBS	N-cyclohexyl-2-benzothiazyl-sulphenamide
CR	Chloroprene Rubber
DEG	Diethylene glycol
DOP	Dioctyl phthalate
EB	Elongation at break
ERBO	Epoxidised rice bran oil
EV	Efficient vulcanization
FFA	Free fatty acid
HAF black	High Abrasion Furnace Black
hr	Hour
HSE	Health, safety and environmental aspects
ISNR	Indian Standard Natural Rubber
MBTS	Mercaptobenzthiazyl disulphide
Mc	Number average molecular weight of rubber chains between crosslinks
MH_F	Maximum torque
min	Minutes

ML	Minimum torque
ML[(1+4)100°C]	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of 4 minutes at 100°C
mm	Millimetre
MOZ	2-morpholino thiobenzo thiazole
MPa	Mega pascal
N/mm	Newton per millimeter
Na22	Ethylene thiourea
NBR	Acrylonitrile Butadiene Rubber
Nm	Newton metre
nm	Nano metre
NR	Natural Rubber
PAH	Polyaromatic hydrocarbons
phr	Parts per hundred rubber/plastic
PVC	Poly vinylchloride
RBO	Rice bran oil
rpm	Revolutions per minute
t_{10}	Scorch time
t_{90}	Optimum cure time
T_g	Glass transition temperature
Tm	Melting temperature
TMTD	Tetramethyl thiuram disulphide
VGC	Viscosity gravity constant
Vr	Volume fraction of rubber
Vs	Molar volume of solvent

w/w	Weight/weight
z	Weight fraction of filler
ρ_r	Density of rubber
ρ_s	Density of solvent
χ	Polymer-solvent interaction parameter

LIST OF PUBLICATIONS

1. The Compounding of Nitrile and Polychloroprene rubbers with rice bran oil, A.P.Kuriakose and Mohan Varghese, Iranian Polymer Journal, Vol.8, No.4 (1999).

2. Utilisation of rice bran oil/epoxidised rice bran oil as process aids in black filled NR-CR blends.

   (Communicated).

3. Use of rice bran oil as a platiciser for the preparation of NBR-PVC blends.

   (Communicated).

4. Epoxidised rice bran oil as a plasticiser/stabiliser for NBR-PVC blends.

   (To be communicated).

5. Use of epoxidised rice bran oil as process aid in Nitrile and Polychloroprene rubber compounds.

   (To be communicated).